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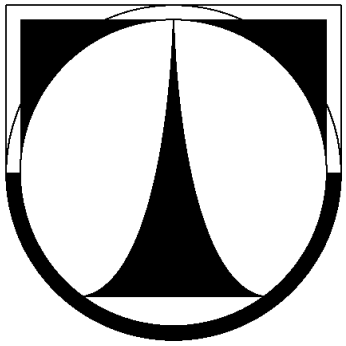

DIPLOMA THESIS

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Technical University of Liberec

Faculty of Textile Engineering

Department of Textile Technology

Textile Chemical Technology

PLASMA PRETREATMENT IN TEXTILE PRINTING

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ABSTRACT.

Synthetic fibers have gained its popularity and constitute a big share of market in textile industry. Due to their hydrophobicity and resistance to chemicals, these fabrics require pre-treatment prior to finishes such as printing. Without having them pre-treated the patterns directly printed with pigment paste have poor color yields and bleed easily. Plasma surface treatment of POP, PES fabrics was carried out in atmospheric plasma with air under different time intervals. After the samples were exposed to plasma were printed with pigment paste. Affectivity of the modification process was determined with hydrophilicity measurements evaluated by means of suction test. Hydrophilicity of individual fabrics has distinct increase after plasma treatment. From the results obtained it can be seen that surface –modified POP, PES fabrics registered enhanced color yields and remarkable good pattern sharpness. XPS and SEM analysis showed that this tremendous improved color performance was assisted by the polar groups induced onto the fiber surface through plasma processing. SEM images exhibited that the rough surface of plasma treated fibers could give more potential for fabric to seize the printing paste .Therefore surface modification using air plasma provides a possibility to process fabric for pigment printing ,which is also advantageous in that ,it is environmentally friendly ,saving energy compared to the traditional pre-processing methods.

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1. Polyethylenepolyvinylchloride	PVC
2. Polytetrafluro-ethylene	PTFE
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5. Nonwoven polypropylene	NWNPOP
6.Woven polypropylene	WNPOP
7. Limiting Oxygen index	LOI
8. Glass transision temperature	T_g
9. Melting temperature	Tm
10. Ethylene glycol	EG
11. Dimethyl terephthalate	DMT
12. Terephthalate acid	TPA
13. Bis-(2-hydroxyethy)-terephthalate	BHET
14. Dimethyle terephthalate	DMT
15. Terephthalic Acid	PTA
16. Atmospheric pressure plasma treatment	APT
17. Dielectric barrier discharge	DBD
18. Diffuse Coplanar Surface Barrier Discharge	DCSBD
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20. Energy of the incident beam	hv
21. Electron binding energy	BE
22. The work function of the spectrometer	(Φ)
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24. X-Ray spectrophotometry	XPS
25. Radio frequency	RF
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30. Carboxylic acid	COOH
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33. Note well	NB
34. Alternting current	AC
35. Contact angle	(θ)
36.Degrees selcius	ºC
37. Low –temperature plasma	LTP
38. High-temperature plasma	HTP
39. Electron energy distribution function	EEDF
40. Kinetic energy	K_E
41. Electron volt	e V
42. Atmospheric pressure plasma	ATM

1 Introduction

Virtually all types of fabric can be printed due to the wide variety of coloring agents, printing machines and formulation aids which make printing process economically viable. Over 95% of printed textiles are now produced using mesh screens in either flat or cylindrical form. Transfer of the print paste through the screen and onto the fabric occurs through the application of pressure, using a metal bar, blade or some form of squeegee. It is crucial to optimize correctly the rheological properties of the print paste formulation for this sort of application**.[1]**

In this work we are looking close at the printability of three synthetic fibers after plasma treatment .These synthetic fibers are classified as thermoplastic polymers since they belong to the same family (thermoplastics) they possess almost similar properties and differ owing to the methods and conditions of production

1.1 Synthetic polymers

Polymers are relatively light, weak organic materials with low melting points that are held together by bonds that are covalent for the most part. They are originated from crude oil.[2]

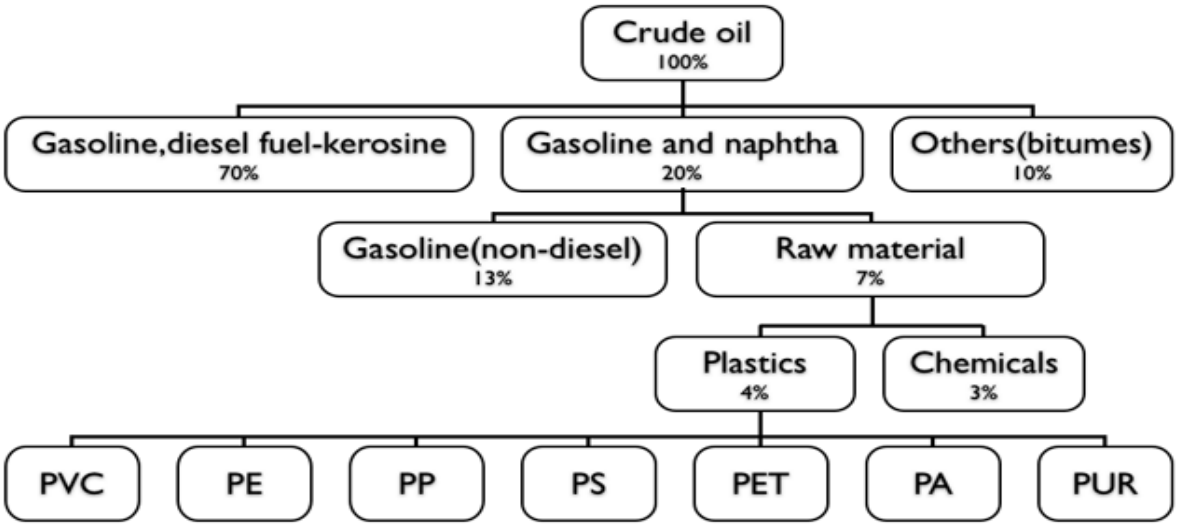


Fig1.1. schematic diagram showing origination of polymers from crude oil[3]

The features that make one polymer sample behave differently than another include ;chemical composition, including the content of co-monomer and its distribution along and among molecules, the distribution of molecular weights, often described briefly by giving two or more average molecular weights, tacticity and long chain branching structure[4]

1.2 Polymerization mechanism[2]

Monomer + monomer →dimer

Dimer + monomer → trimer

Dimer + dimer → tetramer

Trimer +monomer → tetramer

Trimer + dimer → pentamer etc

1.3 Classification of polymers

There are three basic types of polymers:

- Thermoplastics
- Thermosets
- Elastomers

1.4 Thermoplastics

Thermoplastics are distinguishable from thermosets in that they do not curve or set under heat as thermosets do .Thermoplastics soften or melt when heated to a flowable state ,and under pressure they can be forced /transferred from heated cavity into a cool mold. Thermoplastic can be remelted and then rehardened by cooling**[5].**

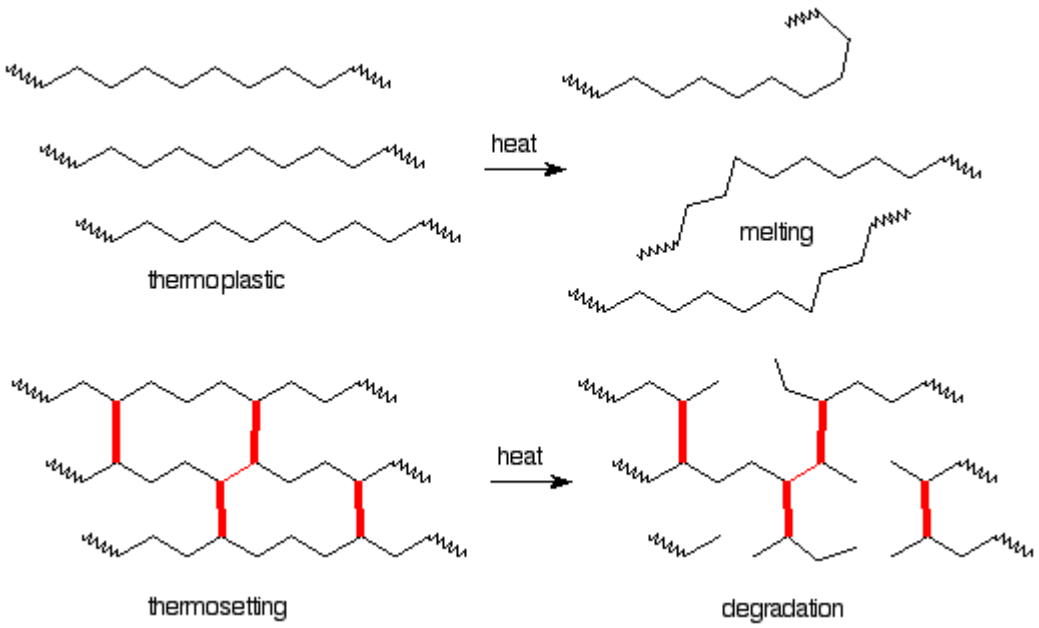


Fig 1.2. Schematic view suggests the difference: according to ref [5]

Thermoplastics consist of long chain molecules that are produces from small molecules (called mers) by polymerization process, where polypropylene is produced from monomers propylene by application of heat, pressure and catalyst. When the resulting polymer is cooled it solidifies. When reheated, thermoplastics will become liquid again .Due to this reversible liquid-solid conversion, Scrap thermoplastic material may be recycled. These thermoplastic materials are ,**polypropylene** polyethylenepolyvinylchloride(PVC) ,polystyrene , polytetrafluro-ethylene (PTFE), **polyesters**, polycarbonates, nylons and cellulosics[6]

1.5 Polymer crystallinity

Polymer crystallinity is one of the significant properties of all polymers .Polymers exist both in crystalline and amorphous form.

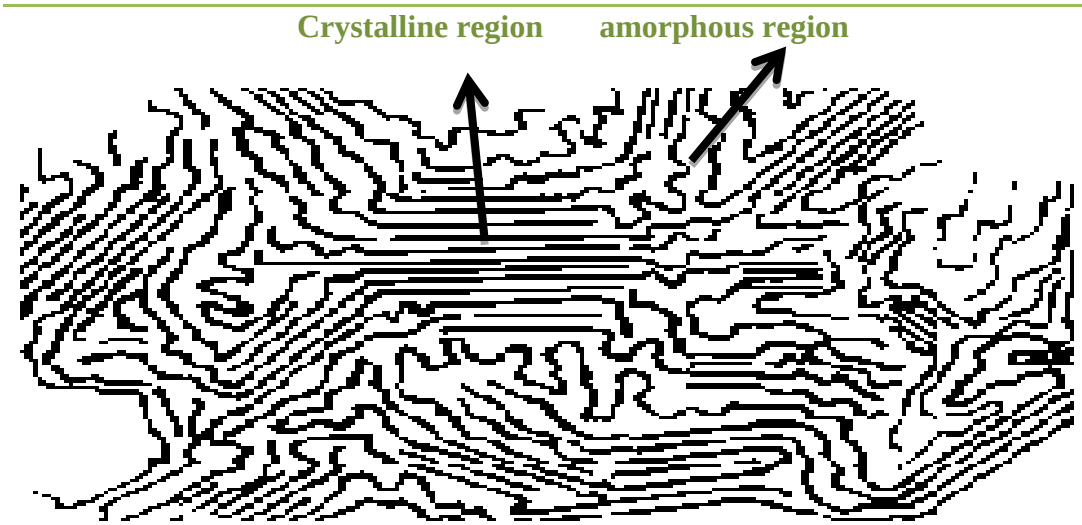


Fig :1.3 Mixed amorphous crystalline macromolecular polymer

It can be seen on the figure above, that part of molecules is arranged in regular order, and these regions are called crystalline regions. In between these ordered regions molecules are arranged in random disorganized state and these are called amorphous regions. This crystallinity influences many polymer properties some of which includes: hardness, modulus, tensile, stiffness, crease, melting point

Practically all polymers always show less than 100% crystallinity. And therefore are called semi crystalline. The degree of crystallinity depends on the disordered regions, also on average molecular weight and molecular weight distribution [7][8]

1.6 Degree of crystallization

All polymers have some degree of crystallinity. Crystallinity vary between 0% (an amorphous polymer)and 80% (a highly crystalline polymer)

The degree of crystallinity of polypropylene is influenced by the production and processing conditions ,such as drawing ratio, drawing speed, and temperature, heat-setting temperature and tension, etc. Due to the already mentioned factors the degree of crystallinity of POP may vary considerable. With commercial fibers it is mostly in the range of 45 – 65 %

The degree of crystallinity of PES can be made with a percent of crystalline domains ranging from 0% to about 55%. Completely amorphous PES is formed by cooling the melt quickly .By prolonging the cooling time ,more molecular diffusion occurs, and crystallites form as the chains become more ordered. The differences in mechanical properties between these forms of PES are substantial, PES with a low degree of crystallinity is used for plastic beverage bottles, whereas fibers drawn from highly crystalline PES are used for textile fibers and tire cords[9]

1.7 General properties of polymers

- Polymers can be very resistance to chemicals
- Generally polymers are very light in mass with varying degree of strength
- Polymers can be both thermal and electrical insulators
- Polymers can be processed in various ways to produce thin fibers or very intricate part.[10]

2 Theoretical Part

2.1 Discovery and development of POP.

Prior to 1954 the attempts to produce plastics from polyolefin had little commercial success. In 1954 Professor Giulio Natta of Milan Polytechnic ,Italy ,discovered that certain Ziegler – type catalysts could bring about polymerization of polypropylene to linear polypropylenes of high molecular weight .It was after the high molecular weight polypropylene was made in 1952 by Fontana ,the polymers obtained were oils and greases. Professor Natta in his research manages to separate his polypropylene into number of polymers, using difference in their solubility. He found that these polymers have different densities ,some have as higher density as 0.91 whereas others were as low as 0.85.He also found that their melting points varies and others crystallized where others remain amorphous. The differences were found even in polypropylene of similar molecular weights.

Polypropylene is a polymeric fiber produced by polymerizing propylene monomers .This polymerization reaction is done under controlled temperatures and pressure .With the addition of a catalyst (Ziegler-Natar or metallocene catalyst) polypropylene is made to be stereospecific. Commercial polypropylene is usually about 90 – 95% isotactic. [**11]**

2.2 Structure of POP fibers

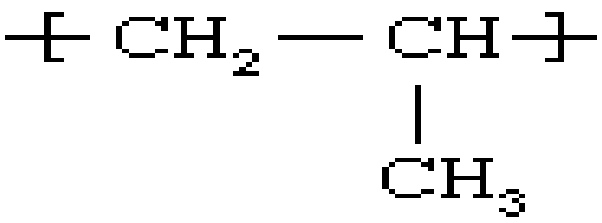


Fig 2.1. structure of polypropylene fiber

POP fibers are composed of crystalline and non-crystalline regions. The spherulites developed from a nucleus can range in size from fractions of a micrometer to centimeter in diameter. The a - axis of the crystal unit cell is aligned radically and the chain axis is homogeneously distributed in a planes perpendicular to this radical direction .Each crystal is surrounded by non – crystalline material. Fiber spinning and drawing may cause the

orientation of both crystalline and amorphous regions the extension is less than 0.5% the spherulites deformation is elastic and no disruption of the structure occurs ,otherwise spherulites are highly oriented in the direction of the force and finally are converted to micro fibrils These highly anisotropic microfibrillar structure leads to anisotropic fiber properties. **[12]** POP consist of flexible chain molecules and a short repeat unit they are highly crystalline by virtue. However, their melting and softening temperatures are too low to enable them to withstand the rigors of laundering, etc. They suffer quite markedly from adverse time effects, and thus find limited applications as commodity textile fibers. POP has high strength and fracture toughness. These attributes, coupled with its very low density (less than 0.9 gcm^{-3}), make it a valuable fiber for ropes and many industrial products. By suitable techniques, the polyolefin may be manufactured with special properties –ultra –high stiffness and strength for example –which render them important as high performance fibers in certain industrial and military textile applications. In this context, they should be really be regarded as second – generation fibers[13]

2.3 Molecular structure of POP

Polypropylene molecule is composed of a certain number of monomers such as propylene, forming a long linear chains arranged in a zigzag manner .The molecular chain consist of carbon atoms connected together through chemical bonds .Macromolecular chain has side methyl groups and possess a tridimensional structure [14].

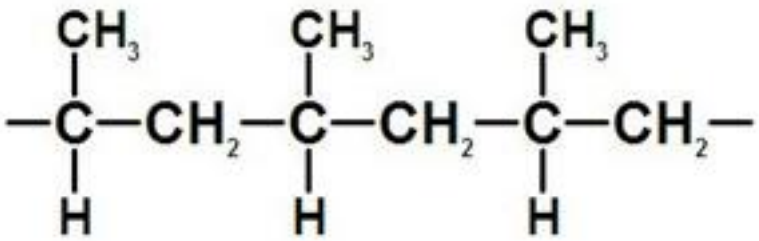


Fig2.2 :molecule of propylene monomer.[**polypropylene (chemical compound)- Britanica online Encyclopedia :Britanica.com]**

2.4 Chemical composition

Polypropylene can assume a different form of stereo regularity which is given by the location of methyl groups towards the plane formed by the zigzag arranged carbon atoms in a linear polypropylene chain.

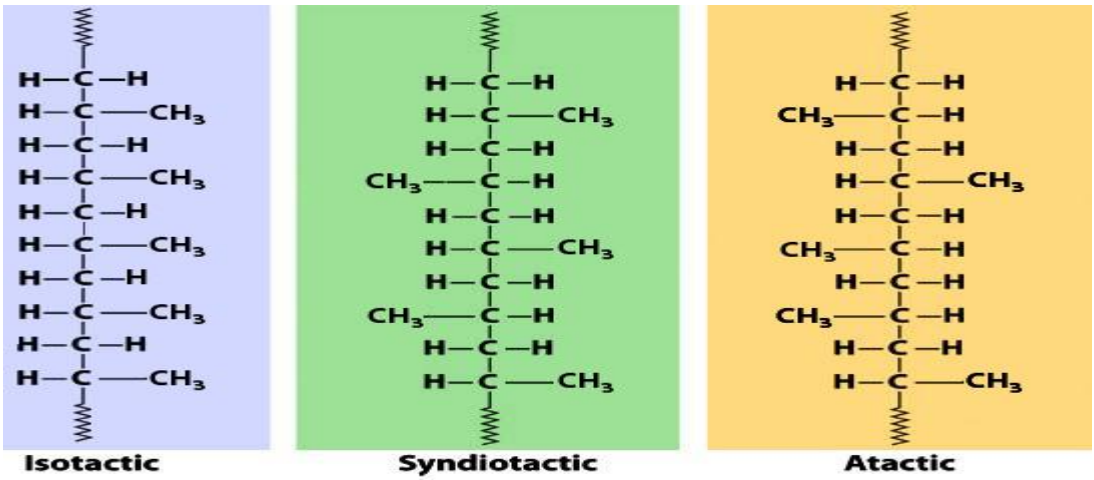


Fig 2.3.molecular configuration of POP

Isotactic structure: all methyl groups occur on the same side and in the same direction to the plane formed by carbon atoms of the linear chain.

Syndiotactic structure : methyl groups are alternately arranged above and below the plane determined by carbon atoms of the zigzag linear chain.

Atactic structure : methyl groups are irregular distributed along both sides of the plane

2.5 Above molecular structure

Crystallization occur between glass transition temperature (Tg) and the equilibrium melting point (Tm) The crystallization rate of PP is fast at low temperature. It is reported that the crystallization rate decreases with increasing crystallization temperature and also decreases with the increase of molecular weight as shown in the figure below. The degree of crystallinity of PP fibers is generally between 50-65% depending on processing conditions .

In isotactic polypropylene the most common commercial form, pendant methyl groups are in the same configuration and are on the same side of the polymer chain. Due to its arrangement, isotactic polypropylene has a high degree of crystallinity.

In syndiotactic polypropylene, alternate pendant methyl groups are on opposite sides of the polymer back bone ,with exactly opposite configurations relative to the polymer chain.It is commercially produced using matallocene catalysts.

Isotactic and syndiotactic structures are capable of crystallizing due to their highly regular backbone; atactic form on the other hand would produce an amorphous material. The

degree of crystallinity present in a polymer is governed by several factors such as the rate of cooling, crystallization kinetics, and the crystallization temperature. Thus, the degree of crystallization can vary greatly for a given polymer and can be controlled through processing conditions.[16]

2.6 Properties of POP.

General properties

Average tenacity :of 4 -7 grams per dinier(high tenacity) It shows resistance towards stress and cracking

Ultimate elongation of 15 – 30%

Shape : it is crystalline in nature and possess regular geometrical shape .

Polypropylene is mildew and insect resistant

2.7 Mechanical properties

Oxygen index	17.4
Tensile Strength	25-33 Mpa
Flexural Modulus	1.2-1.5 Gpa
Elongation at break	150-300%
Strain at yield	10-12%
Moisture Regain	＜0.1%

[17]

2.8 Thermal &thermochemical properties

Thermal properties	
Softening temperature	150˚C
Melting temperature	160-170˚C
Heat conductivity	$11.7*10^{-14}$J $cm^{-1}s^{-1}K^{-1}$

Specific heat	1.9 Jg^{-1} K^{-1}
Shrinkage	
Shrinkage at boil	3 – 9%
Shrinkage at 250˚F	5 - 12.5%

[15]

At temperatures of -70˚C or less – excellent flexibility

At temperatures higher but below 120˚C – fibers remain their normal mechanical

2.9 Electrical properties

Dielectric constant (0.1MHz)	225
Dissipation factor (0.1MHz)	$<$ 0.0002
Specific volume resistivity	$6.5*10^{16}\Omega.Cm$

[18]

2.10 Chemical stability

Excellent resistance to most acids and alkalis with the exception of chlorosulphonic acid and oxidizing agents

Generally good resistance to bleaching agents[19]

2.11 Production of POP (woven &a non woven)

Polypropylene fibers are produced by chain growth polymerization, which involves successive opening of carbon-carbon double bonds. This growth is by addition of monomer units.[19],[20];[21]Then it is further taken to spinning and drawing the process is pretty much the same as the one illustrated in section 3 under production of polyester fibers

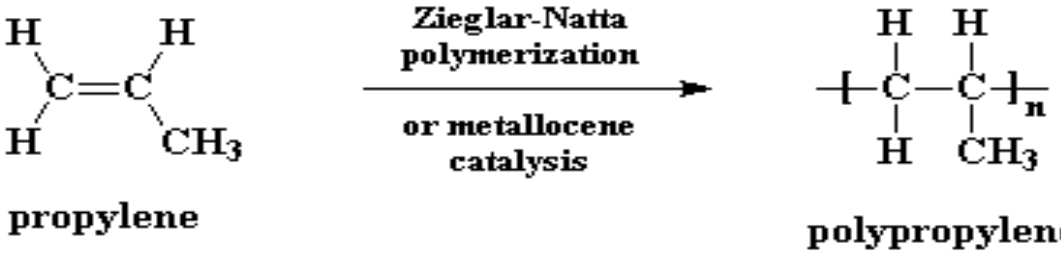


Fig2.4: polymerization of polypropylene.

After spinning and drawing the fibers are then transformed into fabric by using various looms such as weaving and knitting. On the other hand the nonwoven webs are bonded either thermally, chemically or mechanically. Woven polypropylene fabric is produced from continuous filament whereas the nonwoven fabric is produced from separate fibers.

The difference between the two is the fabric technical strength. Since the WN fabric is formed by interlacing the fibers in warp and weft direction and in NWN's there is no interlacing ,the fabric is formed by bonding the webs /sheets .Therefore a woven fabric tend to have more strength than a NWN fabric.

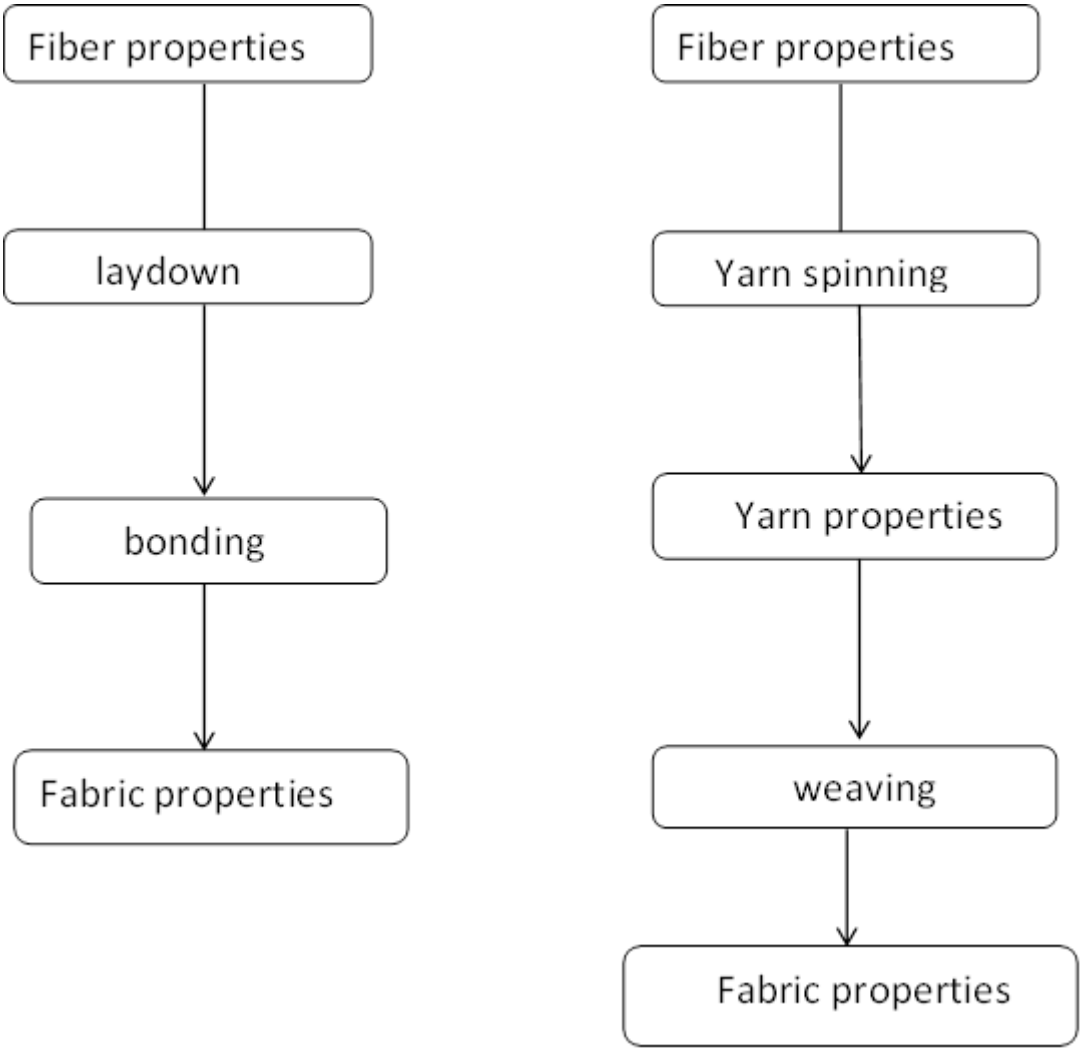


Fig2.5: (a) and (b) illustrating the differences in production of nonwoven fabrics, woven fabrics and the relationship between fiber, yarn, and fabric properties. [15]

2.12 Coloristic properties

Polymers generally ,but notably polyolefin ,have low surface energies and it can be difficult for inks and coatings to adhere to them In the case of polyolefin such as polypropylene (PP) , the problem is particularly severe since this polymer has a surface void polar groups. Thus, only weak physical (dispersion-force) interactions can bond materials such as printing inks to the surfaces.

An additional problem arises in polyolefin caused by their wide molecular weight distribution. The surfaces of polymers such as PP are preferentially made up of low molecular weight chains, creating a cohesively weak boundary layer. Even if strong bonding occurs between polymer and a coating, such as printing ink, the weakness of the boundary layer will lead to easy destruction of the applied ink. Again POP fibers have relatively high crystallinity (50-65%), which partially attributes to its very low dye adsorption. Therefore the surface of PP must be treated prior to coating and the success of those surface treatments have to meet a dual challenge:

1. To introduce polar groups into the polymer surface, thereby bringing into play strong, non – dispersive, forces which strengthen the bond with applied agent such as inks.

2. To strengthen the cohesively weak boundary layer [15][22]

2.13 APPLICATION OF POLYPROPYLENE NONWOVEN FABRICS

Application	Fiber Grade	Industry
Cigarette Filter	Staple fiber 3 denier	Cigarette
Technical filters	Staple fiber 5denier,needle punched nonwoven	Wet filtration, excellent chemical resistance used in water, milk, bear, paints, coatings, petrochemicals, pharmaceuticals, filtration.
POP woven socks	POP film fiber ,with 10-15%LDPE to reduce fibrillation and cost	Fertilizers, Flour, Wheat, Sugar, Cement
Ropes and twines	POP film fiber	Agriculture
POP bale warp	Spun Bonded POP	Synthetic fibers
POP tapes	High modulus POP obtained by increasing draw ratio	Construction material like asphalt and concrete
POP construction /industry fabrics	Filling grade and staple fiber	Construction materials like asphalt and concrete
Substrate fabrics	Nonwoven needle punched 3-4 denier staple fibers	Furniture fabrics as backing material for visual furniture fabrics, it serves as reinforcement .Also used for wall covering luggage ,table – clothes ,tarpaulins, and automobile
Outdoor Applications	Heavy denier containing stabilizers, UV absorber, etc	sports

2.14 Polyester fibers.

2.15 Discovery & development of PES

The British chemist, John Rex Whinfield and James Tennant Dickson employed by Calico Printer's Association of Manchester invented '"polyethylene terephthalate " in 1941 after advancing the early research by W. H. Carother's who first developed polyester in 1928. Polyethylene terephthalate is the basis of synthetic such as polyester ,Dacron, terylene . They created the first polyester fiber called Terylene in 1941 in cooperation with other inventers (W. K. Birtwhistle and C. G. Ritchiethey). DuPont after forming an alliance with the ICI (Imperial Chemical Industries) produces the second polyester known as Dacron. DuPont purchased the U.S. right for further development in 1945. In 1950 a pilot plant at the SEAFORD ,Delaware , facility produced Dacron (polyester) fiber with modified nylon technology [23]

DuPont's polyester research lead to a whole range of trademarked products ,example is Mylar which was born in 1952, an extraordinary strong polyester (PET) film that grew out of the development of Dacron in the early 1950s[24]

Polyesters are created from chemical substances found in petroleum and are manufactured in fibers, films, and plastics. It is manufactured by two routes, Trans esterification of dimethyl ester with di-ol to form an intermediate di-ester and oligomers, followed by polycondensation to form the polymer or direct esterification of di-acid with di-ol, followed by polycondensation. **[25]**

2.16 Structure of polyester fibers

Fig 3.1 structure of polyester fibers

2.17 Molecular structure

The molecular mass of fiber – forming PET for textile application lies between 20000 and 40000. Polyester is a long chain polymer chemically composed of at least 85% by weight of an ester and dihydric alcohol and terephthalic acid . [26]

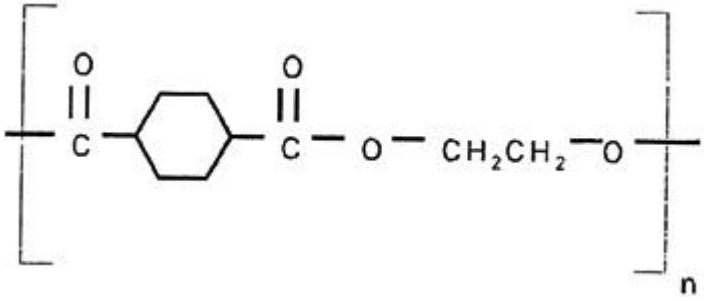


Fig 3.2.molecular structure of PES[27]

2.18 Microscopic appearance of PES fibers

Polyester fibers are smooth and rod like with an even diameter. Their diameter usually ranges from 12-25micrometers (10 – 15 denier). The fibers generally have circular cross-section Some types have a trilobal cross-section Staple fibers is crimped .They may or may not contain pigment.

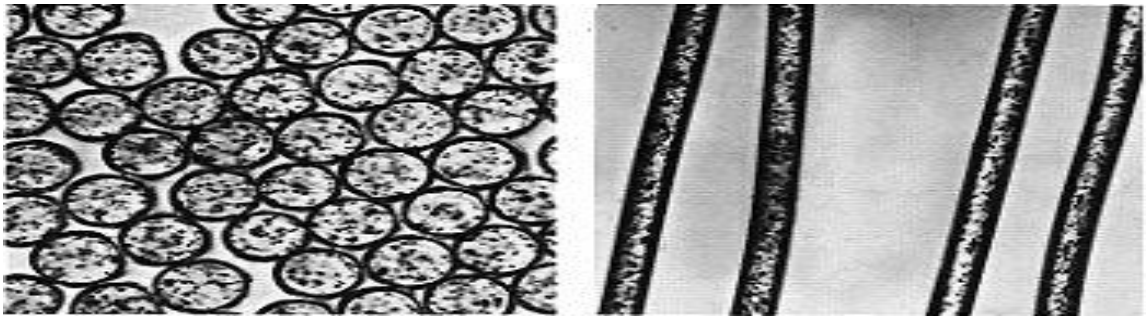


Fig3.3: cross-section and longitudinal view of polyester[28]

2.19 Above molecular structure

Crystalline aromatic polyesters have sufficient high melting point to make them suitable for textile fibers

The fibers are approximately 35%crystaline and 65%amorphous.

2.20 Chemical composition

Polyesters are the most commercially important "melt – spun" synthetics. Polyester fibers are formed from a chemical reaction between an acid and alcohol. In the reaction, two or more molecules combine to make a large molecule whose structure repeats throughout its length. Polyester fibers can form very long molecules that are very stable and strong **[15]**

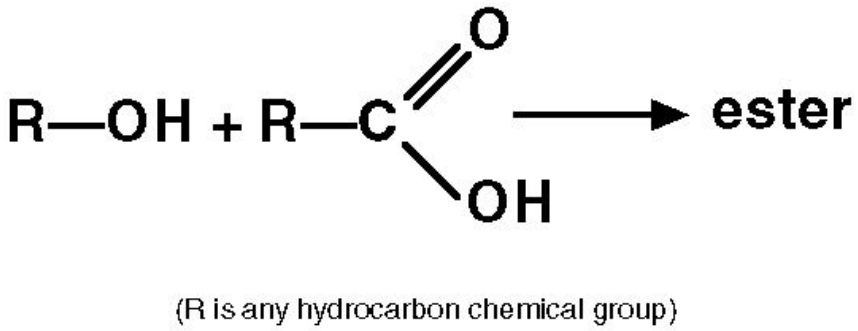


Fig 3.4: chemical composition of PES

2.21 Polyester production

The principle ingredient used in the manufacturing of polyester is ethylene, which is a derivative of petroleum. It is produced by a chemical process called polymerization where ethylene is the polymer and the chemical building block of polyester [29]

Polyester is produced by one of several method depending on the form polyester will take and end use of the product. The four basic forms are filament, staple, tow, and fiberfill. In the filament form, each individual strand of polyester fiber is continuous in length, producing smooth-surfaced fabrics. In staple form, filaments are cut to short, predetermined lengths, in which polyester is easier to blend with other fibers. Tow is a form in which continuous filaments are drawn loosely together. Fiberfill is the voluminous form used in the manufacture of quilts, pillows and outerwear. Filament and staple form are frequently used Polyester filament yarn and staple are produced either by direct melt spinning of molten polyester from the polymerization equipment or by spinning reheated polymer chips [30]

Production of polyester fibers start by producing

- Raw materials,
- Step growth polymerization,
- Product

Raw materials

Polyesters are commercially produced from ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalate acid (TPA). Both processes first produce the intermediate bis-(2-hydroxyethy)-terephthalate (BHET) monomer and either methanol (DMT process) or water (TPA process) . BHET monomer is then polymerized under pressure with heat and catalyst to produce PES [31],[32]

Terephthalic Acid (PTA), is produced directly from p-xylene with bromide controlles oxidation

- Dimethyle Terephthalate (DMT) produced in the early stages of esterification of terephthalic acid
- Ethylene Glycol (EG) generated as an intermediate product by oxidation of ethylene. Further ethylene glycol is obtained by reaction of ethylene oxide with water.

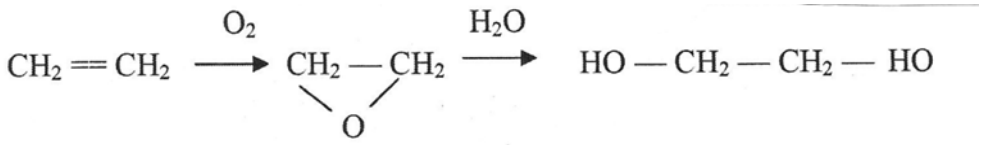


Fig3.5: production of ethylene glycol.

The polymerization has two steps: esterification reaction and condensation reaction

There are three steps in the synthesis of polyester

2.21.1 Condensation Polymerization:

When acid and alcohol are reacted in a vacuum at high temperatures it results in condensation polymerization. Once the polymerization has occurred the material is

extruded onto a casting in the form of a ribbon. Once cool ,the ribbon hardens and is cut into chips

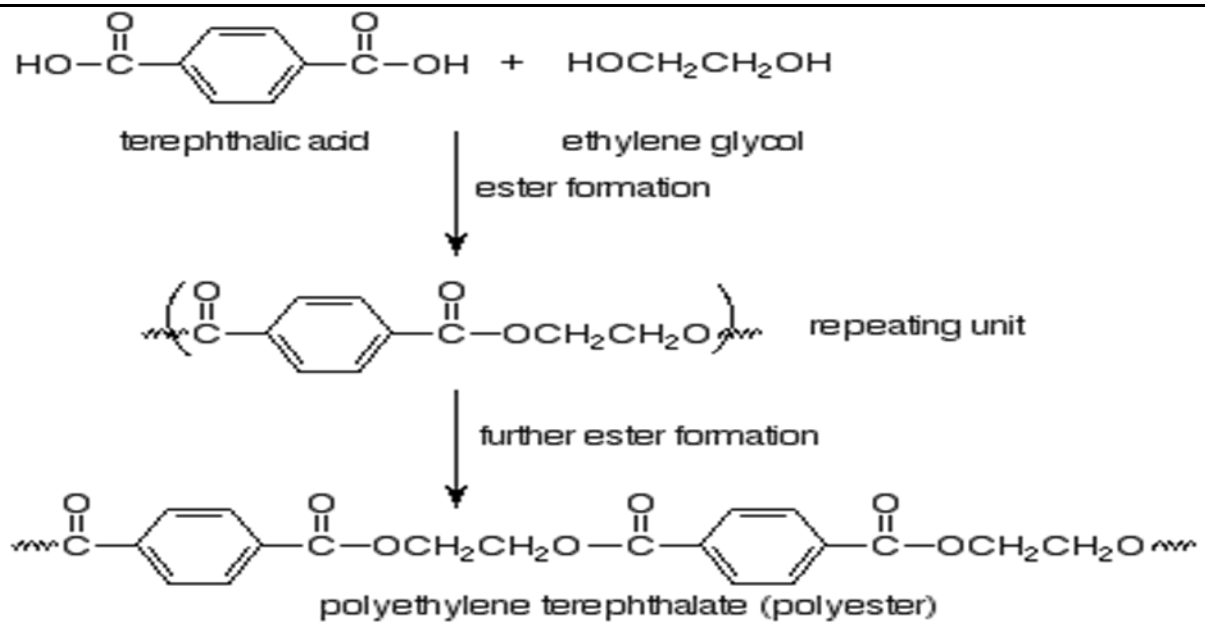


Fig : 3.6.polymerization of PES.[15]

2.21.2 Melt – spun fiber**:**

The chips are dried completely .Hopper reservoirs are then used to melt the chips. A unique feature of polyester is that it is melt –spun fiber. The chips are heated/melted at 260-270˚C, extruded through spinnerets and cools upon hitting the air .It is then loosely wound around cylinders.

2.21.3 Drawing

the fibers consequently formed are hot stretched to about five times their original length. This helps to reduce the fiber width. This fiber now is ready and wound into cones as filaments. It can also be crimped and cut into staple lengths as per requirements.

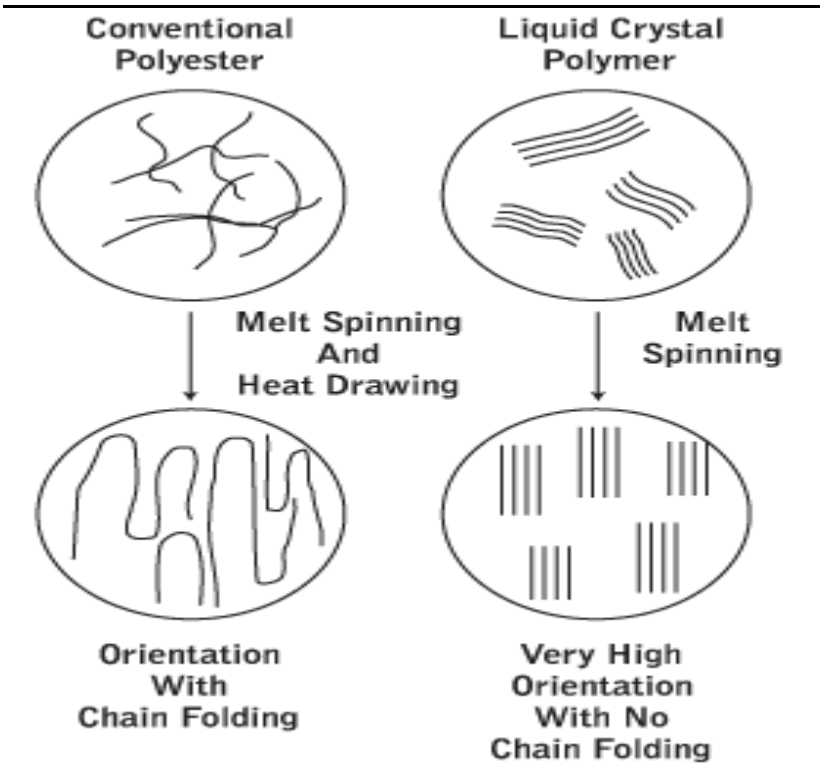
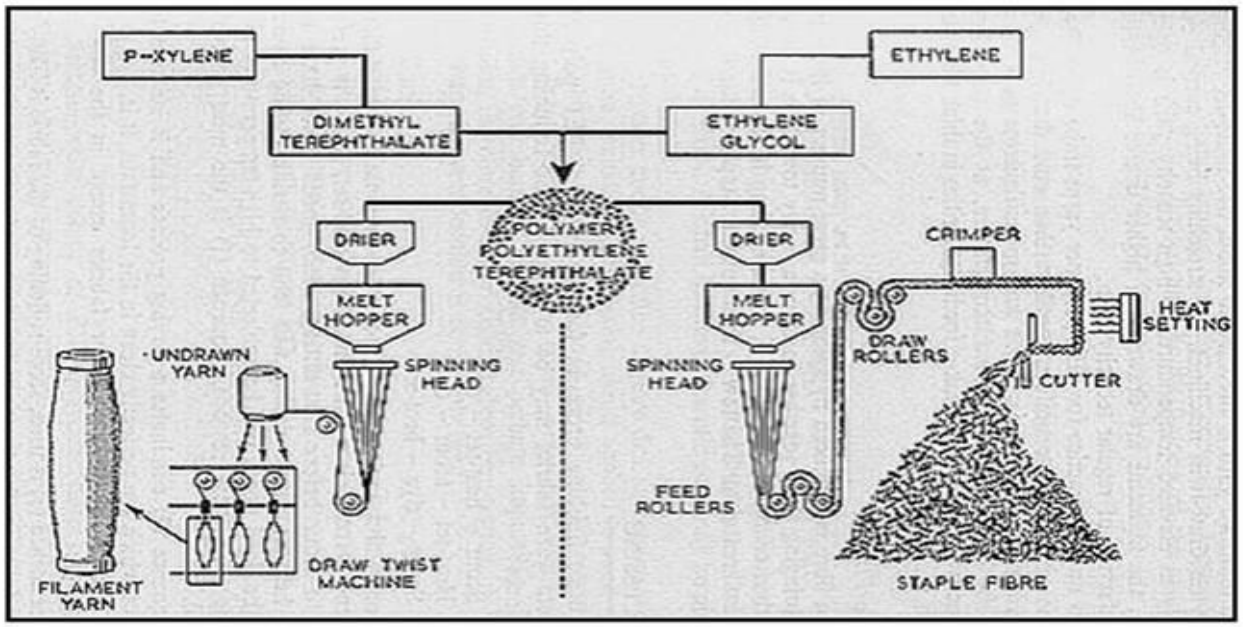


Fig 3.7 : schematic presentation of molecular chain orientation during drawing[33]



[15] [34]

Fig 3.8 : schematic representation of industrial process for synthesis of poly (ethylene terephthalate)

2.22 Polyester properties

2.22.1 Mechanical properties

Tensile strength	3.8 – 7.2 $cNdtex^{-1}$
Elasticity	50 -70%
Wet strength(% of dry)	100%
Wet elasticity	19 – 23%
Electric recovery	86 – 90%
Elasticity modulus	1300 $cNtex^{-1}$
Density	1360 – 1380 Kgm^{-3}
Degree of polymerization	100 - 150
Elastic recovery	85 – 90 %

2.22.2 Thermal properties

Glass transition temperature (Tg)	77 - 80˚C
Softening temperature	260˚C
Sticking temperature	230 - 240˚C
Melting temperature (Tm)	250˚C -270ºC
Limited Oxygen Index(LOI)	20.6%
Thermal conductivity	0.218 $Js^{-1} m^{-1} K^{-1}$
Heat capacity	1130 $JKg^{-1}K^{-1}$
Shrinkage at 100˚C and 150˚C	3% & 10%
Shrinkage at boil	6%
Moisture absorption	0.4%

Effect of low heat :-at 40˚C the tenacity increases by 6% consequently its extensibility decreases by 30% relative to the tenacity at 20˚C.

At 100˚C : The tenacity increases by 50% and extensibility decreases by 35%

Effect of high temperature: at 180˚C tenacity is 50% compared to the tenacity at normal temperature .Heated at 150˚C tenacity is about 85% of its original strength

Flammability: low flammable

Effect of sunlight: has high resistance to degradation by light

2.22.3 Electric properties

- Very good electric insulator
- Tendency to form electrostatic charge
- Low friction coefficient(T= 0.174)

2.22.4 Chemical stability

Acids: - it is resistant to majority of organic acids and mineral

- Under extreme conditions cause gradually degradation of a Fiber.

Alkalis: - shows excellent resistivity under moderate conditions.

2.22.5 Coloristic properteis

Due to the close packing of the macromolecules in synthetic fibers, polyester fibers are difficult to dye [35]. On the other hand the polar group which is brought about in a structure by an ester group makes it not so difficult but only selective pigments that can be use

2.22.6 Uses and applications

Polyester is used in the manufacture of many products including clothing, home furnishings, industrial fabrics, computer and recording tapes, and electrical insulation.

2.22.7 Advantages over traditional fabrics

It absorbs oil; this property makes it the perfect fabric for the application of water, soil, and fire –resistant finishes. Its low absorbency also makes it naturally resistance to stains .Polyester clothing can be preshrunk in the finishing process, and thereafter the fabric resist shrinking and will not stretch out of shape .The fabric is easily dye able , and not damaged by mildew. Textured polyester fibers are an effective, monalle2rgenic insulator, so the material is used for filling pillows, quilting, outerwear, and sleeping bags.[36

2.23 Plasma treatment

2.24 What is plasma

Plasma is an ionized gases .Hence they consist of positive and negative ions , electrons as well as radicals .The term plasma is often referred to as the fourth state of matter. [37]

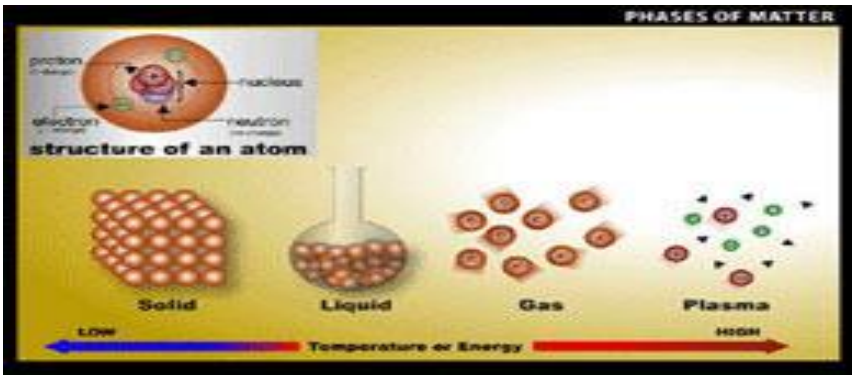


Figure: 4.1 illustrates how atoms or molecules are converted into positively charged ions [39]

As the temperature increases, molecules, become more energetic and transform matter in the sequence: solid, liquid, gas, and finally plasma, which then justifies the title "fourth state of matter" [38]

Plasma among the phases of mater has neither definite volume nor a definite shape just like gases. [39]

Much of the visible matter in the universe is in the plasma state. Stars, as well as visible interstellar matter in the universe are in the plasma state. The ionization degree can vary from 100% (fully ionized gases) to very low values (partially ionized gases).[40]

2.25 Plasma classification

Plasmas are frequently subdivided into low (LTP) and high-temperature plasma (HTP) ,and a further subdivision relates to thermal and non-thermal plasmas (see the flow diagram below) [41]

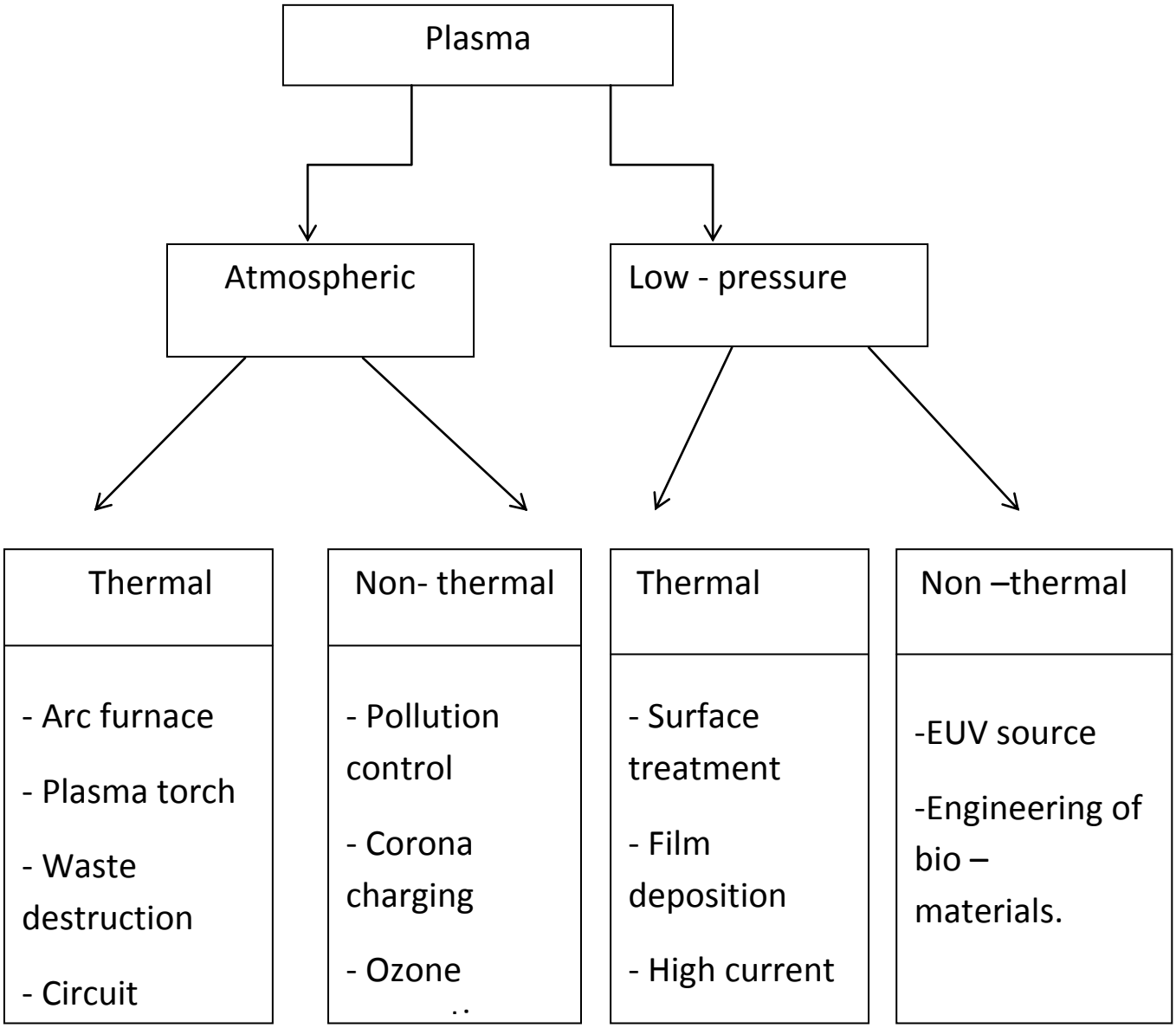


Fig :4.2 Overview of plasmas and their application.[42]

In plasma state, electrons obtain high energies. If all species (electrons, molecules, ions etc.) in the plasma obtain a thermal energy distribution at the same high temperature, the plasma is called thermal, indicating that the plasma is in equilibrium. If the electrons and other species are not in thermal equilibrium i.e. if only the electrons have high energies, the plasma is called non – thermal [43]

2.26 Properties of thermal and non-thermal plasmas

Table 4.1: properties of thermal and non-thermal plasmas[44]

$T_e = T_h$ High electron density :$10^{21} – 10^{26}$ m^{-3} Inelastic collisions between electrons and heavy particles create the plasma reactive species whereas the elastic collision heat the heavy particles (thus ,electron energy is consumed) E.G. Arc plasma $T_e = T_h \approx 10.000K$	$T_e » T_h$ Lowe electron density: $< 10^{19}$ m^{-3} Inelastic collisions between electrons and heavy particles induce the chemistry. Heavy particles are slightly heated by a few elastic collisions, which is a reason why the electrons energy remains very high Glow discharges $T_e \approx 10.000 – 100.000K$ $T_h \approx 300 – 1000K$

2.27 Plasma generation

Plasma has many uses as a result there are several means for its generation, however, one principle is common to all of them: **there must be energy input to produce and sustain it**. Plasma can be generated by supplying energy to a neutral gas causing the formation of charge carriers. When electrons /photons with sufficient energy collide with the neutral atoms and molecules in the feed gas (electron-impact ionization or photoionization), electrons and ions are produced in the gas phase.

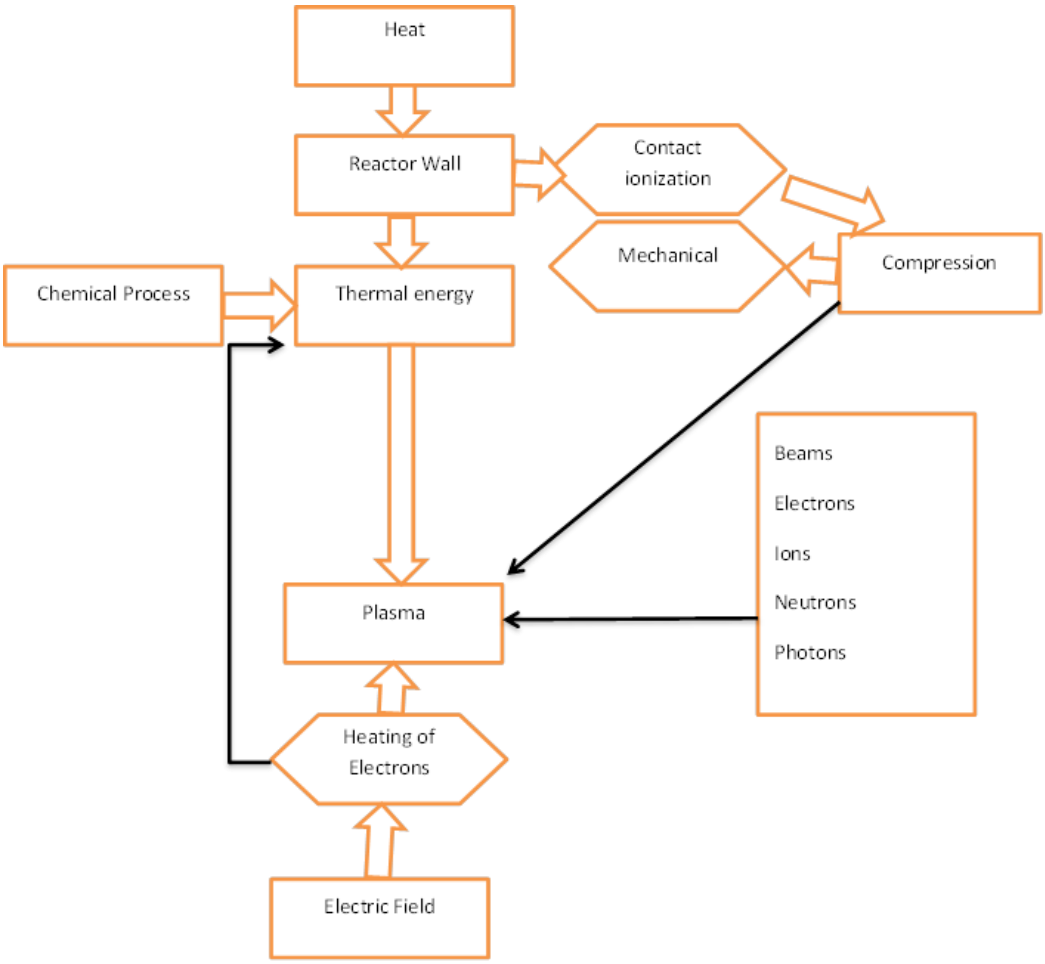


Fig4.3 : principle of plasma generation [44]

4.2.Plasma kinetics

4.2.1.Important plasma properties

- Debye shielding
- Plasma frequency
- Plasma parameters

2.28 Debye shielding

Shielding effect is a characteristic of all plasmas. It does not occur in every medium containing charge particles. Shielding of electrostatic field occur as a consequence of collective effects of the plasma particles. Charged particles align themselves in such a way as to effectively shield any electrostatic fields within a distance of Debye length

Debye length is a measure for electrostatic screening in plasma. It plays a major role in describing plasm action. A Debye sphere is a volume whose radius is the Debye length. The electric potential around a test charge is given by the following equation

Debye length is given by the equation:

$$\lambda_D = (\epsilon_\circ kT / \eta_e e^2)^{1/2} \qquad (4.1)$$

It is required that physical dimensions of the system be large compared to Debye length:

1st criterion

$$L \gg \lambda_D \qquad (4.2)$$

2nd criterion

$$\eta_e \lambda_D^3 \gg 1 \qquad (4.3)$$

The higher the free charge carrier concentration the smaller the Debye length and the better the screening. At very low temperatures there is less thermal motion and thus the screening is also much better.

Plasma approximation is another important parameter which measures the ratio of the mean interparticle potential energy to the mean plasma kinetic energy. It should be much lesser than 1 ($g \ll 1$) and it is defined by

$$g = 1/\eta_e \lambda_D \qquad (4.3)$$

[38],[45],[46]

2.29 Plasma frequency

Plasma electron frequency is a measure of plasma oscillations of the electrons. It is largely compared to the electron – neutral collision frequency which is a measure of collision frequency between electrons and neutral particles.

$$\omega_{pe} = (4\pi n_e e^2/m_e)^{1/2} = 5.64 \times 10^4 n_e^{1/2} \mathrm{rad/s} \qquad (4.4)$$

Ion frequency

$$\omega_{pe} = (4\pi n_i Z^2 e^2/m_i)^{1/2} = 1.32 \times 10^3 Z\mu^{-1/2} n_i^{1/2} \mathrm{rad/s} \qquad (4.5)$$

2.30 Plasma parameters

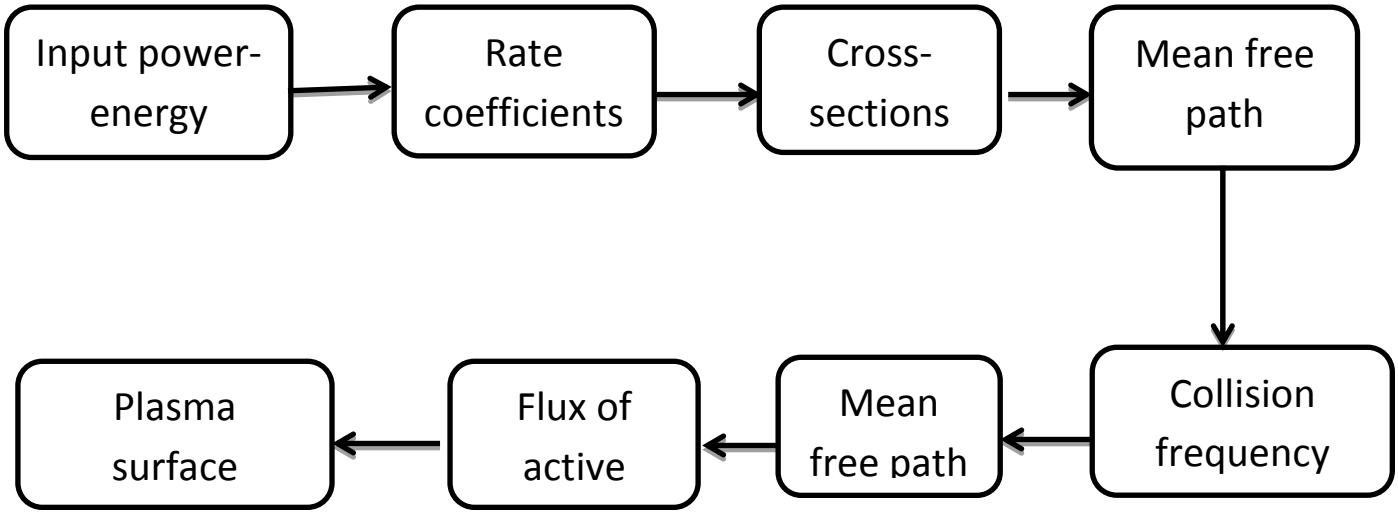


Fig4.4: Kinetic parameters of plasma processing

Fig: mechanism of the plasma chemical process

Mean free path (λ) : $\lambda = 1/n\sigma$ (4.6)

n =3.220x10^{22} p (*Tor r*)

σ = cross-section

n = number density: n = f (T)

these free mean path are divided to 3 where there is a

neutral – neutral free path — p =100 Pa , T =300K → λ ~ 100 μm – 1mm

p = 1 Pa , T =300K → λ ~ 10 mm or longer

ion – neutral mean free path — p = 100 Pa ,T =300K → λ ~ 50 μm – 1mm

p = 1 Pa ,T =300K λ < 2cm

electron – neutral free path — p = 100 Pa ,T =300K → λ ~ 1 mm – 1cm

p = 1 Pa ,T =300K → λ ~ several centimeters (RF / ECR)

2.31 Ionization process

Electrons are the first in getting energy from electric fields, due to their low mass and high mobility .Electrons in turn transmit the energy to all other plasma components, providing energy for ionization, excitation, dissociation and other plasma chemical processes. How fast a process would be is determined by the number of electrons consists of enough energy to do work. The rate of work can be described by means of the electron energy distribution function (EEDF) f (ε): this is a probability density for an electron to have energy ε. EEDF is strongly dependent on electric field and the gas in plasma. It is determined by the quasi – equilibrium Maxwell-Boltzmann distribution function:

$$f(\varepsilon) = \sqrt[2]{\frac{\boldsymbol{\varepsilon}}{\boldsymbol{\pi}(\boldsymbol{kTe})3}} \exp\left(-\boldsymbol{\varepsilon}/kT_e\right) \qquad (4.7)$$

where k is Boltzmann constant

Te =electron temperature

ε = energy of an electron

mean electron energy given by :

$$\varepsilon = \int_0^{\infty} \boldsymbol{f}()\boldsymbol{d} = \frac{3}{2}\boldsymbol{Te} \qquad (4.8)$$

NB: Numerically in most plasmas the mean electric value is from 1 – 5 eV

Ions are heavy particles therefore they cannot receive high energy directly from electric fields owing to intensive collisional energy exchange with plasma components.

2.32 Collisions in the plasma reactor

Elastic collision: $K_{E\ (before)} = K_{E\ (after)}$ (4.9)

- This collision result only in geometric scattering and redistribution of kinetic energy between the colliding partners

Typical value for cross sections of elastic:

- Electron –neutral collisions for electron energy of 1 to 3 e V $\approx \sigma = 10^{-16}$ to 10^{-15} cm^2 ; $k = 3*10^{-8}$ cm^3 /sec
- Ion –nuetral collisions at room temperature ~ σ 10^{-14} cm^2 ;$k = 10^{-9}$ cm^3 / sec.

  k= reaction rate coefficient [38]

  .

Inelastic collision: $K_{E\ (before)} \neq K_{E(after)}$ (4.10)

- Like ionization ,result in energy transfer from kinetic energy of colliding partners into internal energy, sometimes the internal energy of exciting atoms /molecules can be transferred back into kinetic energy particularly kinetic energy of plasma electrons.

Super elastic collisions: momentum is redistributed between the colliding particles and where the internal energy from one / both of participants is transferred to the final total kinetic energy of the participants.

2.33 Formation of active species

Primarily the function of plasma discharge in processing applications is to generate the ions and chemically active sites required. The species results from inelastic collisions.

Electron based reaction

Conditions: Electron kinetic energy (thermal) 2 – 10 Ev,ion energy 0.025Ev(room temperature of neutral gas).

Ionization: (4.11)

$$e + Ar \rightarrow Ar^{+} + 2e$$

$$e + O2 \rightarrow O2^{+} + 2e$$

Dissociation: (4.12)

$$e + O2 \rightarrow O + O + e$$

$$e + CF4 \rightarrow CF3 + F + F$$

$$e + CF3 \rightarrow CF2 + F + e$$

$$e + CF \rightarrow C + F + e$$

Dissociation ionization : (4.13)

$$e + O2 \rightarrow O^{+} + O + 2e$$

$$e + CF4 \rightarrow CF3 + F + 2e$$

Dissociation attachment: (4.14)

$$e + SF6 \rightarrow SF6^{-} \rightarrow SF5^{-} + F$$ [47],[48]

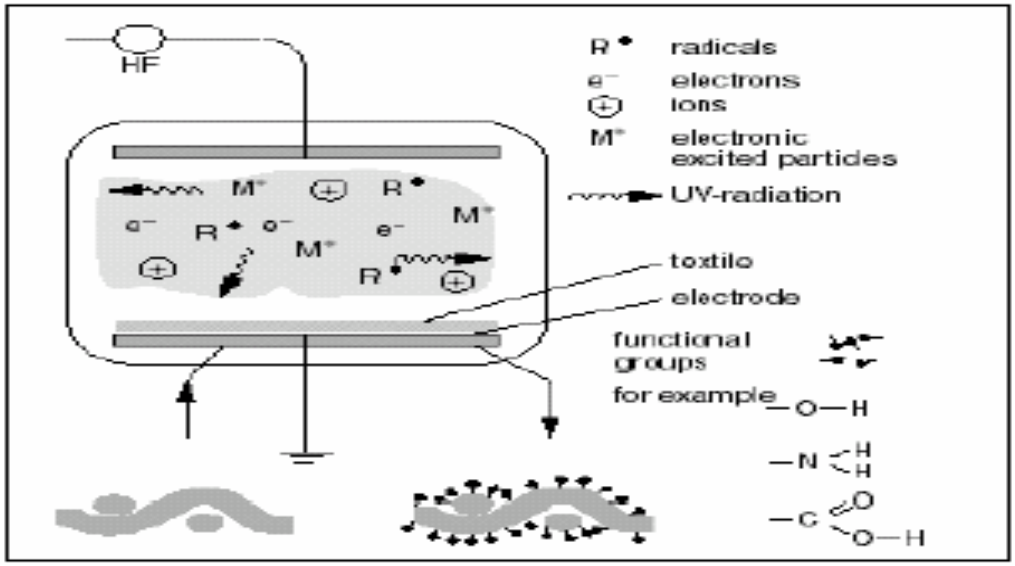


Fig4.5: schematic view of plasma device and different reactive species[49]

2.34 ATM Plasma System:

The most used in textile industry is the ATM Plasma system

Atmospheric pressure plasma treatment (APT) is very attractive technology for surface functionalization. ATP allows to create a uniform and homogeneous high density plasma at atmospheric pressure conditions and at low temperature using AC power and a broad range of inert and reactive gases.

2.35 Applications

:can be used for treating & modifying the surface properties of both organic and inorganic materials. APT system can be used for wide variety of applications including:

- Treatment of polymer films ,fabrics, paper , wool , foils
- Plasma grafting and plasma polymerization.
- Ashing organic materials in the microelectronics industry
- Barrier layer deposition for the packaging industry
- And sterilizing biologically contaminated materials

The newly developed APT

- produces a uniform and homogeneous plasma
- Allows use of variety of gases.
- Ideal for treating polymer films; uniform treatment ; enhances surface energy of the films thereby improving the wettability , printability and the adhesion; no backside treatment
- no vacuum chamber and pumps are needed
- simple and rugged construction

2.36 Operation modes

The APT could be used in the following modes of operation

- cold flame with controlled chemistry
- reduced ozone corona
- corona with controlled gas chemistry : chemical corona: [50][51],[52]

4.4.3:Table 4.2 : Types of gas plasma applied and their effects

GAS PLASMA	EFFECT
Argon	Increase surface roughness
Oxygen	Modification of surface chemical groups Better wetting
Fluorocarbons	Polymerization Improved water repellency
Ammonia, carbon dioxide	Modification of surface chemical groups

[48]

2.37 Atmospheric pressure plasma sources

2.37.1 Arc discharge

a high power thermal discharge of very high temperature (~10.000K) It can be generated using various power supply .Commonly used in metallurgical processes

2.37.2 Corona discharge

:non – thermal discharge .It can be generated by applying a high voltage to sharp electrode tips .Used in ozone generators and particle precipitators.

2.37.3 Dielectric barrier discharge (DBD)

: non- thermal discharge, generated by applying a high voltage across small gaps.it has similar applications to corona discharge and is widely used in the web treatment of fabrics .It's application to synthetic fabrics and plastics functionalizes the surface and allows for paints and to adhere.

2.37.4 Capacitive discharge:

non-thermal plasma .It is generated by the application of RF power -13.56MHz to one powered electrode with grounded electrode held at a small separation distance on the order of 1 cm .It is stabilized using noble gas such as helium/argon[52];[53]

2.38 Gas plasma reactor

The reactor is a combination of a vacuum chamber with vacuum pump and purge plumbing ,a source of electromagnetic energy (rf generator) , process gas sources abd a system controller to orchestrate the process.

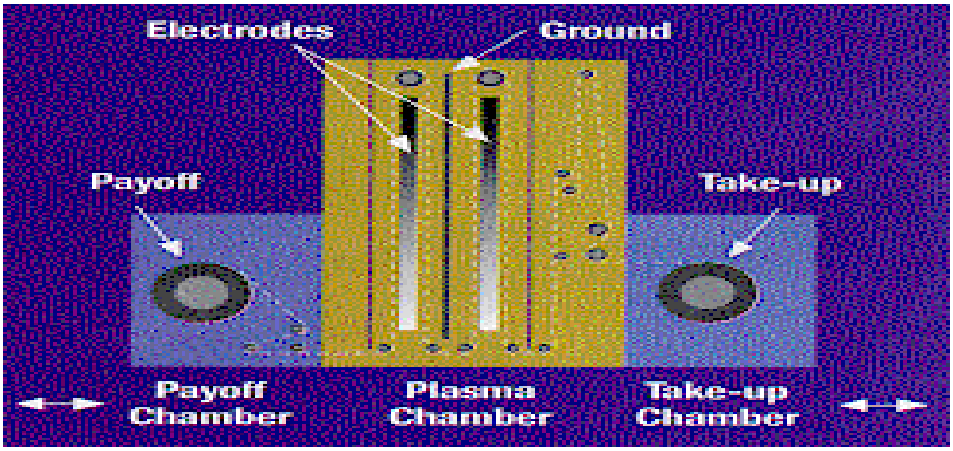


Fig4.6 : plasma reactor

2.39 Process steps

A substrate is loaded in the payoff chamber and threated through the chamber to the take-up reel. The plasma treatment operateion is then initiated and entirely controlled by the push of a single button.

1.Pump down to predetermined vacuum pressure (base pressure); 2. Introduce a process gas and stabilization at a desired process ;3).initiate the plasma by providing rf energy; 4).transport product through the system ;5).after treating the desired length, shut rf power and process gas delivery;6).pump down to base pressure to eliminate residual process gas(es);7).vent to atmosphere;8).remove treated product . [54]

2.40 Plasma surface interaction

Plasma processes encompasses:-plasma cleaning, plasma surface activation, plasma coating and plasma etching.

2.40.1 Cleaning process:

Cleaning of surfaces means the removal of all possible undesired residues, such as oxides, metallic and organic contaminants or photoresist in the semiconductor industry**.** In this process inert gases such as (Ar, He) and oxygen plasmas are used .The process cleans ,via ablation, organic contaminates such as oils and other production releases on the surface of most industrial materials. These surface contaminants as polymers, undergo abstraction of hydrogen with free radical formation and repetitive chain scissions, under the influence of ions, free radicals and electrons of the plasma, until molecular weight is sufficiently low to boil away in the vacuum

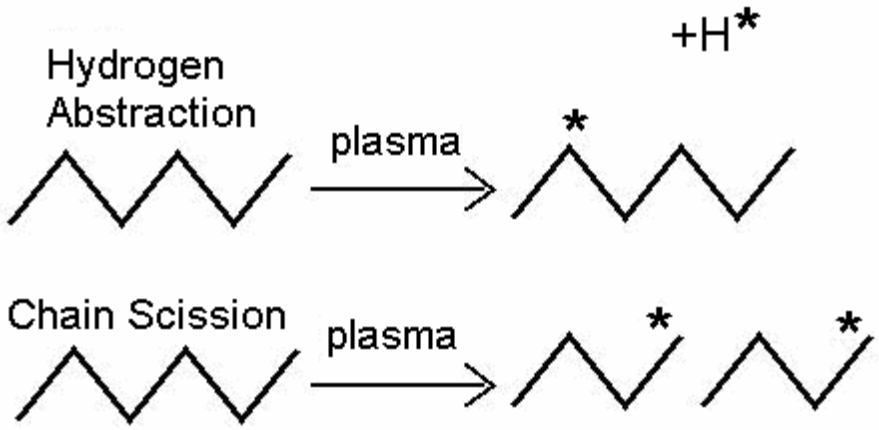


Fig 4.7:Free radicals formation by means of plasma action .Plasma can abstract hydrogen from the polymeric chain or can split chains.[55],[56].

2.40.2 Plasma surface activation

Activation process: -surface is only activated when it is treated with a gas , such as air ,nitrogen, oxygen , argon, ammonia or nitrous oxide, water - vapor, and others, that does not contain carbon.(carbon dioxide, methane) The major results is the incorporation of different moieties of the process gas onto the surface of the material under treatment .Take for instance the surface of a hydrocarbon (that means it contain only carbon and hydrogen in its structure)with a plasma treatment , the surface may be activated anchoring on it functional groups such as hydroxyl l, carbonyl, peroxyl, carboxylic ,amino and amines. Hydrogen abstraction produces free radicals in a plasma gases and functional groups on the polymeric chain. Polymers activated in such a manner provide greatly enhanced adhesive strength and permanency, which is a great improvement in the production of technical fabrics

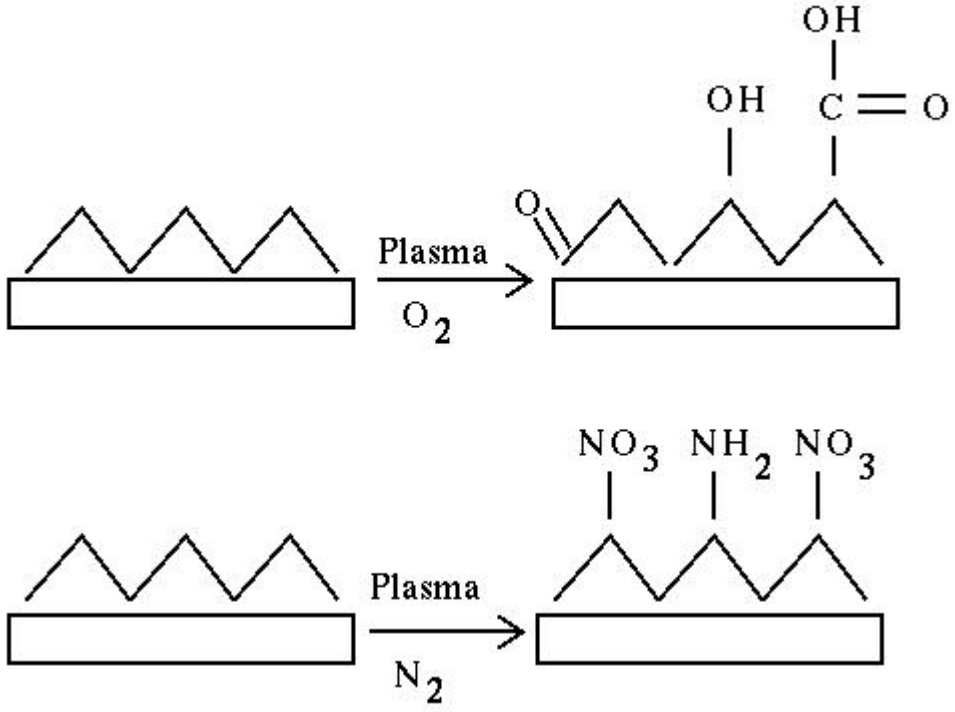


Fig4.8:example of surface activation by substituting hydrogen in a polymeric chain with other groups such as O,OH,COOH,NO_3 NH_2 etc

Each gas produces a unique plasma composition and results in different polymer surface properties.

Grafting process

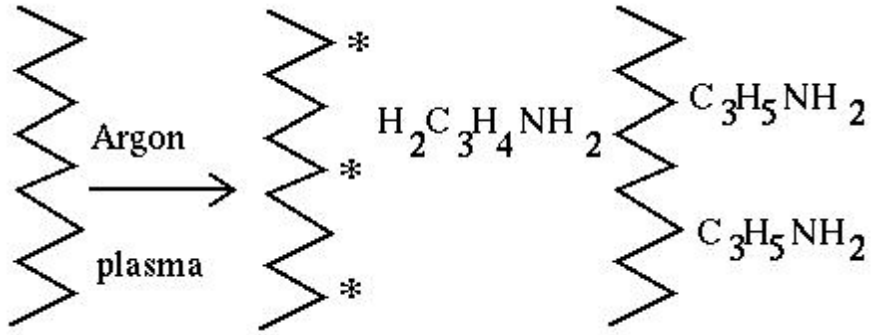


Fig 4.9: Grafting

Grafting of a monomer on the surface, plasma produces' radicals on the chain and monomers are grafted on the surface.

The process is used when nonfunctional groups are required.

4.5.4. Applications of plasma processes.

2.40.3 Applications of plasma processes

Cleaning	**activation**	**Coating**
Removal of greases, oils.	Pre-treatment before printing	Deposition of hydrophobic layers
Removal of silicon's	Pre-treatment of plastic for gluing	Deposition of hydrophilic layers
Pretreatment of surfaces when printing /gluing and before painting	Pre-treatment of plastic for finishing	Deposition of protective barrier layers

[56],[57],[58]

2.40.4 Effects of plasma treatment on textiles

Enhence mechanical properties*:-* Softening of cellulosic fibers (cotton) and cellulose-based polymers, with a treatment by oxygen plasma. Reduced felting of wool with treatment by oxygen plasma.

Crease – resistance of wool,cotton ,silk when treated with nitrogen and dipped in DMSO.

Electrical properties:-antistatic finish of material such as rayon when treated with plasma consisting of chloro (chloromethyl) dimethylsilane. [59],[60],[61]

2.40.4.1 Enhance hydrophilic properties

2.40.4.1.1 Wetting:

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting is determined by a force between adhesive and cohesive forces.

Table4.3: Various degrees of wetting are summarized in this table

Contact angle	Degree of wetting	Strength of solid/liquid interactions	Strength of liquid/liquid interactions
$\theta = 0$	Perfect wetting	Strong	weak
$0 < \theta < 90°$	high wettability	Strong weak	Strong weak
$90° \leq \theta < 180°$	low wettability	weak	strong
$\theta = 180°$	perfectly non-wetting	weak	strong

2.40.4.1.2 Contact angle:-. a quantitative measure of the wetting of a solid

Contact angle , θ , is defined geometrically as the angle formed by a liquid at the three phase boundary where liquid, gas and solid intersect. See figure bellow

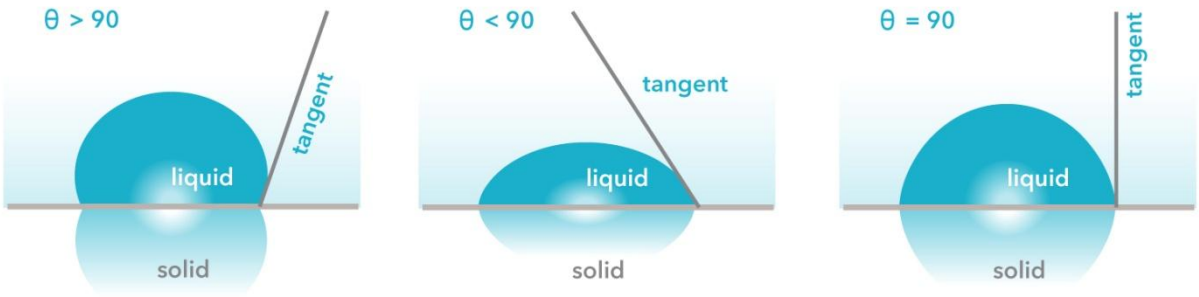


Fig4.10: showing the intersection of a liquid, gas and a solid.

The low value of contact angle (θ) indicates that the liquid spreads, or wets well, whereas the high contact angle indicate poor wetting. The shape of the droplet is determined by the Young's relation.

It is measured using a contact angle goniometry. It is not limited to a liquid/vapor interface; it is also applicable to the interface of two liquids or two vapors.[62],[63].

NB: since the contact angles are sensitive to contamination, external factors like temperature, humidity, solid surface roughness and static electricity etc. will affect the results .Therefore it is important to measure the contact angle in a controlled environment.

2.40.4.1.3 Dyeing/printing

- Improves capillarity of cotton and wool and increase depth of dyeing on synthetic material i.e. polyester. treatment :oxygen .and argon[59],[64],[65]

2.41 Polymers under plasma treatment

For any gas composition, three simultaneous processes alter the molecular layers of the polymer

2.41.1 Ablation:-

is literally boiling off of the outer molecular layer of the polymer surface by the bombarding energetic plasma particles. Charged particles (electrons, free radicals, and ions) and ultraviolet photons break the covalent bonds of the polymer backbone, resulting in fragmented polymer chains of a much lower molecular weight. As long molecules become shorter, the volatile oligomer and monomer byproducts ablate and are swept away with the outgoing vacuum pump exhaust. Ablation can be very effect in cleaning metal foils or fabrics as well as conventional polymer films, removing contaminants such as mold- release or process oils. Or removing weak boundary layers.

2.41.2 Crosslinking

forming covalent bonds between adjacent polymer chains, ideally in an atmosphere such as argon or helium. The inert gas is ionized and covalent polymer bonds are broken at the polymer surface, 10 to 40 Å deep. Since there are no free radicals scavengers in an inert gas, one of three things can occur in the inert plasma: the dissociated molecule can simply revert to its previous state by recombining, it can react with an adjoining free radical within the polymer chain, forming a double or triple bond, or it can form bond with a nearby free radical on an adjacent chain (this occurrence is crosslinking). Crosslinking may strengthen certain polymers, retard the migration of additives (blooming), and /or modify the permeation characteristics.

2.41.3 activation

results when different atoms or chemical groups from the plasma are added to the surface molecule of the treated plastic surface. As with ablation, surface bombardment by energetic particles breaks the polymer chain or extracts pendant group or atom such as hydrogen, forming free radicals.[55]

2.42 Durability of treatment

2.42.1 How long does it last

Parts remain active for few minutes up to several months, depending on the particular material that has been plasma treated Polypropylene for example can still be reprocessed several weeks after treatment.

2.42.2 Advantages of plasma treatment

- It is applicable to most of textile materials for surface treatment.
- Optimization of surface properties of textile materials without any alternation of the inherent properties of the textile materials
- It is dry textile treatment processing without any expenses on effluent treatment
- It is a green process without generation of chemicals, solvents or harmful substances. The consumption of chemical is very low due to the physical process.
- It is applied to different kinds of textile treatment to generate more novel products to customers need and requirement.
- It is a simple process which could be easily automated and perfect parameter control.

2.43 Disadvantages

Disadvantages varies depending on the reactor used ,application and the substrate. The major disadvantage lies on the price of the instrument . the price increases as the size increase.

2.44 Conditions and safetey

- Plasma treatment eliminates safety risk associated with worker exposure to dangerous chemicals
- Plasma processing contained within a vacuum chamber ,with little or no direct exposure

Operates at near – ambient temperatures with no risk of heat exposure

- Uses no harmful chlorinated fluorocarbons ,solvents, or acid cleaning chemicals
- The EPA has classified most plasma processes “green” environmentally friendly process

2.45 PRINTING

2.46 What is printing

Printing is described as dyeing in a localized area to create patterned design. Textile printing uses the same dyes or pigments applied to produce dyed fabric .The same principles of specific dye classes having select fiber affinities and the general fastness characteristics apply equally to printing and dyeing. Dyes / pigments used in dyeing are usually in water bath solution .when the same dyes or pigments are used for printing, they must be thickened with gums or starches to prevent the wicking or flowing . Some dyes cannot be used in printing paste due to:

Insufficient solubility and low color yield.

The application of a pattern to fabric by the use of dyes, pigments or other colored substances may be affected by a variety of hand or machine processes

Dyes are fiber specific:

Dyes are chosen for printing based on the fibers, which compose the textile fabric. i. e a 100%cotton fabric can be printed with reactive dyes, vat dyes, or any dye that works for cotton. Cotton /polyester blend requires two dye types combined in the printing paste. One type for the cotton fibers, such as reactive, and one type for polyester fibers, such as disperses.

Textiles pigments may also be used .They are not dyes but colorants and require a binder or glue to fix them to the surface of the textile fibers. Unlike dyes, pigments are not fiber specific therefore a 60/40 cotton /polyester can be printed with a single pigment .They work equally well on 100%cottonand various blends.

The textile fabric has to be very absorbent so that the locally printed ink adheres fast on the fiber even if the printing is very fast. It also needs a high surface stability, to avoid the distortion of the pattern. This distortion can be caused by a distortion of the warp and weft of the textile fabric during the printing cycle.

Printing process uses various printing techniques such as stencil printing, rotary printing etc.[66],[67]

2.47 Steps in printing

- Preparation of print paste
- Printing of fabric
- Drying
- Fixation of dyestuff
- Washing – off

NB: not all fabrics are after washed. In applications where pigments are printed on finished fabric, after washing of the print is not normally performed.[68]

2.48 Preparation of printing pastes

Types of specific formulation used depends on the fiber, the colorant system used, printing method (direct, discharge, resist or transfer printing) fixation method and to some extent the type of printing machine employed. Nevertheless, the paste should be capable of being applied to variety of synthetic and natural fibers and be wash fast and dry clean resistant, once the applied to the textile

2.49 Primary chemicals in printing pastes

The most important ingredients of any printing paste formulation are the colorants and the thickener system. As mentioned before dyes are fiber specific. The dyes for synthetic fibers are dispersing dyes

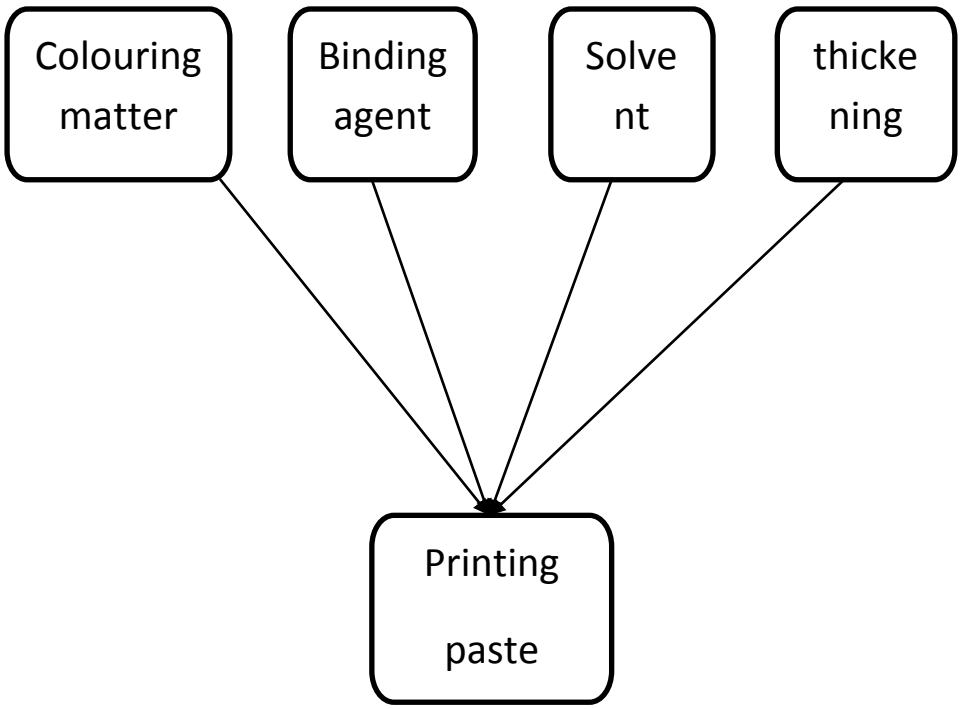


Fig 5.1 summary of important chemicals for printing

[69],

2.49.1 Coloring matter

Coloring agents are dyestuffs e.g pigments or dyes .Dyes are soluble in the application solution On the other hand pigment are not so soluble [70]

2.49.1.1 Pigments

Coloring components are inert materials. They are adhered to the surface of the substrate by the binding system without in themselves reacting with the substrate. After print application and drying, pigment printed fabrics are normally heat cured to facilitate binder action. A fabric is finished without after washing. Pigment print films are pseudo plastic in nature. Due to this reason they tend to present a slightly surface coated look. Color flow and system printing properties are suitable for all printing techniques. Fastness of pigment prints is also quite acceptable for most end uses [70]

2.49.2 The most important pigments

Black and grey –these are extremely permanent. Mostly Carbon Black(PB7) ranging from channel black to furnace black

Blue and Greens –extremely permanent . almost exclusively the various shades of Copper Phthalocyanine(PB15series) with greens being chlorinated.(PG7.PG36)

Reds and Oranges – The highest permanence are with reds found among the Vat pigments (PR149) and the linear Quinacridones (PR192). With Oranges, Benzimidazolone (PO36) and Perinone (PO43) are outstanding.

Yellows – well known are variations of Benzidine (AA,OT,MX,HR) out off these only HR (PY83)withsome sort of permanency

Violets –the outstanding violets are bluish Carbazole Violet (PV23) and the reddish Quinacridone Violet (PV19),[71],

2.49.3 Binders

It is high molecular weight film forming material aid in bonding pigment to the fiber. The binder is important in determining the fastness properties. The ideal binder system would provide fastness rubbing properties. Pigment binders are made using polymer latexes .The monomers contribute specific properties to the final polymer (binder).

2.49.4 Thickeners

The thickener system is the crucial component of print paste. The purpose of the thickener system is twofold:-

- The thickener gives the print paste the proper viscosity or flow characteristics. So the color can be applied uniformly and evenly.

- It holds the color in place so that one color paste can be applied adjacent to another without the color bleeding into the other. With dyes the thickener also holds the color in place after drying until the printed fabric goes through the fixation process where the dye is released from the thickener and is diffused into the fiber. Thickeners used with dyes are then washed off the fabric before, any chemical finishing is performed. However, the thickener applied with a pigment system will remain with the print, as no after washing is required. There is a wide range of thickener materials available these include: alginate,

natural vegetable gums, synthetic polymers, or even foams. These materials show sensitivity to factors such as temperature, pH, and salt content [67];[71]

The ideal thickener for print paste formulation should meet the following requirements:

- Maintain all the components of the paste in a stable suspension.
- Minimal viscosity change on storage.
- Inert to the other components of the print paste.
- Easy removal during the washing process.
- Must flow through the screen during printing, but recover viscosity rapidly once the shear force is removed.
- Give a sharply defined print without any diffusion into adjacent areas(flushing)

Good even color (levelness) of the final print[67]

2.49.5 Printing process

The actual printing process involves the application of a printing paste on a substrate with the aid of selected machinery.

2.49.6 Drying

After printing the textile material is wet and it requires to be dried at temperatures relatively low

2.49.7 Curing/fixation.

In printing specifically pigment printing, if a textile is washed soon after printing and drying, the colorant will be washed away. Therefore requiring an appropriate fixing technique .Fixation in pigment printing is done by simply baking the fabric. At adequate temperatures the binder forms a film that incorporates the pigment particles and glues to the surface of the fiber .Consequently if the temperature and pH conditions are suitable, cross-linking between the binder molecules is achieved.[71],[72]

There are two main types of paste used in textile printing

- Pigment emulsions
- Plastisol paste

Emulsion paste

- Used for direct printing of material
- Suitable for all types of fibers
- Able to dry by evaporation at room temperature
- Able to cure at 160°C for 2 – 3 minutes, to achieve washing and dry – cleaning fastness.

Pigment dispersions are specifically formulated dispersions for textile printing, usually base on organic pigments.

Pigment emulsion formulation

Table5.1 : typical formulation of a pigment emulsion printing paste (based on aqueous dispersion)

Components	Ratio
Pigment dispersion	5.0 %
Binder	15 %
Catalyst solution	3.0 %
White spirit	62.0 %
thickener	4.0 %
Emulsifier	1.0 %
Water	10.0 %

2.49.8 Water based pigments

In water based pigments the white spirit is replaced with water. The binder could be an acrylate copolymer which is capable of crosslinking in the presence of a catalyst under heat .The catalyst use is ammonium salts of inorganic acids such as di-ammonium phosphate or ammonium thiocyanate. Specific properties of printing pastes are controlled by the addition of auxiliaries such as lubricants, accelerators, thickeners humectants or softeners for example.[73]

2.49.9 Plastisol paste

- Used for direct printing of material and for transfer pastes
- Based on a vinyl resin dispersed in plasticizer.
- Characterized by virtually 100% non – volatility, no solvent is present
- Used frequently for printing on dark /dark colored fabrics

2.49.10 Factors affecting the printing paste passing through the screen

- The viscosity of the print paste: higher viscosity causes a comparatively slow passage of a printing paste.
- The number of squeeze strokes – if the number is more the printing paste will pass slowly
- The squeeze angle and pressure- pressure enhance the speed of print paste
- The speed of the squeeze strokes – higher squeeze strokes speed means higher amount of print paste to pass.
- The mesh (thread/inch)/raster (thread/cm) of the screen –the more mesh a screen will have, the more print paste will be passed.
- The fraction of open area in the screens-the more open areas the more print paste will pass over the screen.
- The hardness /X-section of squeeze blade –it is better to have harder screen to pass the print paste smoothly
- The hardness of the printing table –affects the print paste to pass smoothly [67]

2.50 Printing methods

There are three basic methods of printing

1. Direct printing
2. Discharge
3. And resist

The fourth and new technique is transfer printing

2.50.1 Direct printing

It is the most common approach to apply a color pattern onto a fabric .It may be done on white fabric or over a previously dyed fabric. If done one colored fabric, it is known as overprinting. The desired pattern is produced by pressing dye on the fabric in a paste form.

2.50.2 Discharge printing

In this technique, the fabric is dyed in piece and then it is printed with a bleaching agent that destroys the color in the designated areas. Sometimes the base color is removed and other color is printed in its place. The printed fabric is steamed and then thoroughly washed.

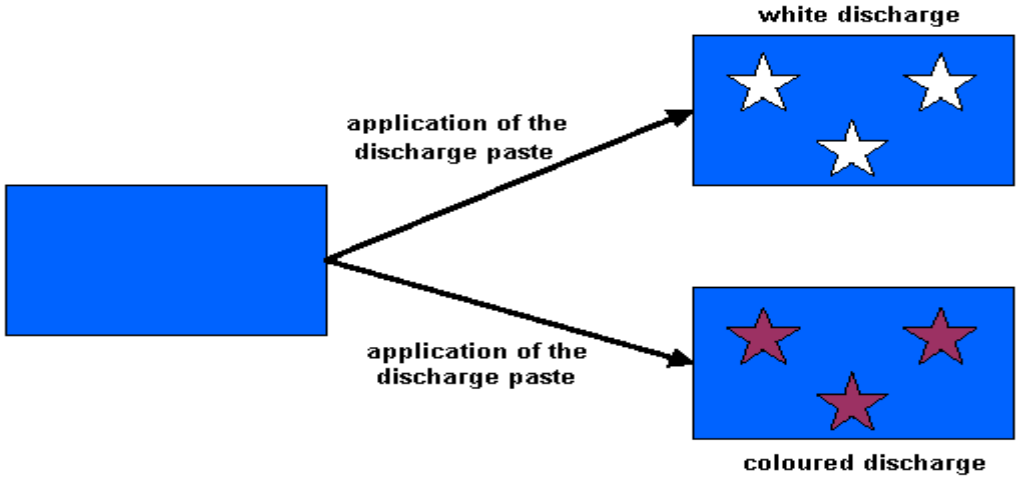


Fig 5.2.discharge printing

2.50.3 Resist printing

In resist printing a resist paste is fixed onto the fabric and then it is dyed. The dye affects only those parts that are not covered by resist paste. After dyeing, the resist paste is removed leaving a pattern on the background of the fabric.

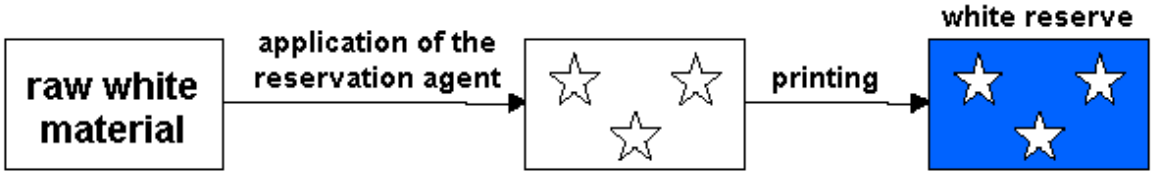


Fig5.2:resist printing

There are several other method for printing in which one of the above three techniques is used, these methods include:-

Block Printing ,Roller printing, Duplex printing , Stencil printing , **Screen printing** ,Transfer printing, Jet spray printing, Electrostatic printing , Photo printing, Batik dyeing, Tie dyeing, Airbrush (spray) painting and ,Digital printing.[67][74]

2.51 Printing technique

2.51.1 Screen printing

This technique is the most common form of textile printing. It involves the application of the printing paste through fine screen placed in contact with the fabric to be printed. A design is created in reverse on the screen by blocking areas of the screen with a material such as an opaque paint. The screen is then placed over the fabric and the printing paste is forced through the open areas of the screen using flexible synthetic rubber / steel blade known as squeegee.

It is done either with flat or cylindrical screens made of silk threads, nylon, polyester, or metal. The printing paste or dye is poured on the screen and forced through its unblocked areas onto the fabric based on the type of screen printing used it is known as either flat screen printing or rotary screen printing.[75]

2.51.2 principle of screen printing

Principle:-The fabric is first glued to a moving endless belt. A stationary screen at the front of the machine, is lowered onto the area that has to be printed and the printing paste is wiped with a squeegee .Afterwards the belt with the fabric glued on it is advanced to the pattern – repeat point and the screen is lowered again .The printed fabric move forward stepwise and passes through a dryer. The machine prints only one color at a time.[76]

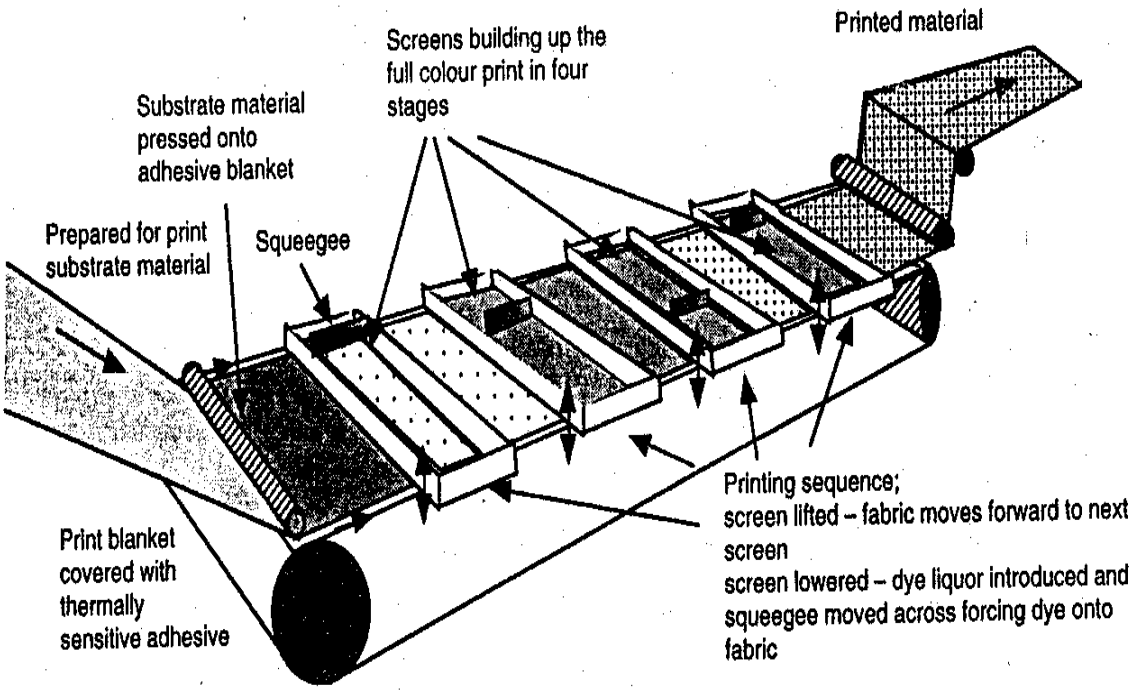


Fig 5.3: flat screen printing process

Flat screen printing machine can be manual, semi automatic or completely automatic

2.51.3 Types of screen printing

Hand screen printing

Semi –automatic screen printing

Fully automatic screen printing

2.51.4 Manual : Hand screen printing

The prim paste is spread across the screen by hand with a (rubber) squeegee blade forcing the paste through the screen. This manual method may cause irregularities.

The amount of paste which is pushed through depends on factors such as:

- the mesh (raster) or number of threads per unit length, i.e. per inch (cm); this gives the fineness of the screen and affects the printing sharpness

- the fraction of open or non-covered area of the screen, determined by the mesh, yarn diameter and subsequent treatments such as calendering,
- the hardness and cross-section of the squeegee,
- the viscosity of the print paste: a paste with low viscosity passes through the screen pores more readily,
- the hardness of the table: a hard table requires a soft squeegee,
- the number of squeegee strokes (usually 2 to 4) and the squeegee angle and pressure,
- the speed of the squeegee strokes.

2.51.5 Semi-automatic flat screen printing

The squeegee is moved across the screen mechanically. It is impossible to reach a considerable speed of working with this method.

2.51.6 Automatic flat screen printing

The use of hydraulic main drive is replaced by an electronic main drive .which improves speed up to 28.5meters per minute with a one –meter repeat.

These machines show a no of features namely:

Electric squeegee drive system, Automated and self –leveling squeegee pressure adjustments for uniform print paste distribution, Automatic flash cure systems attached to the print pallets, Quick push button pallet change, Individual push button lock/unlock of screens, Motorized automatic screen positioning ,incorporated with digital design memory, Control keypads at very print station with all main machine functions, Touch screen user friendly computerized main machine controls and diagnostic fault detection system[77]

2.51.7 Components of screen printing

5.7.1Stencil:-This consists of a frame onto which a mesh is attached under tension. The mesh is coated /covered with a photosensitive material. The image to be printed is created photographically on the stencil leaving open areas of mesh through which ink passes. The stencil is also known as the screen.

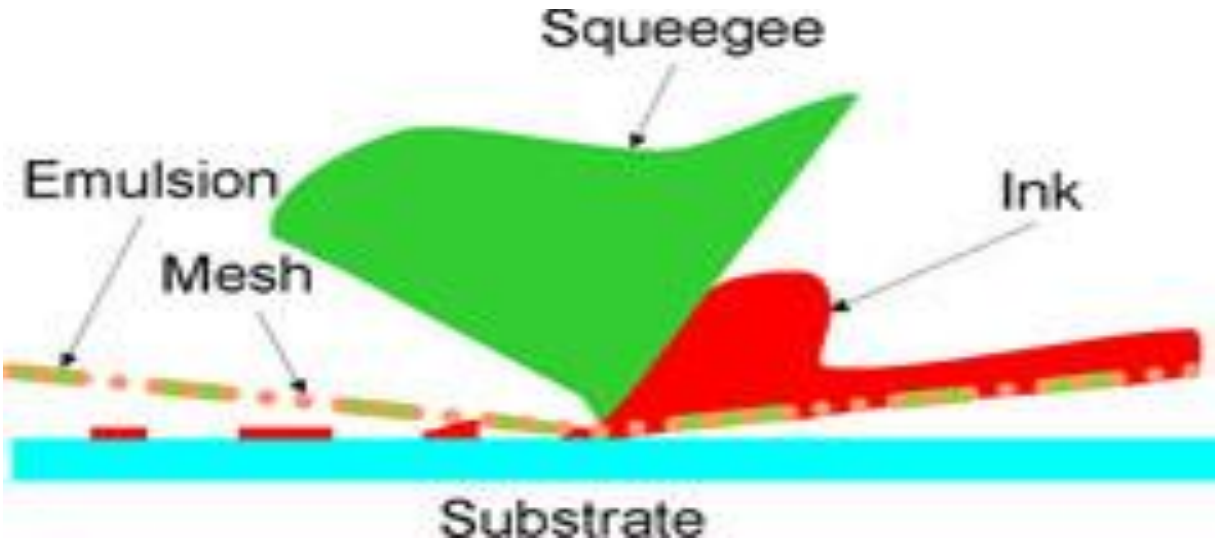


Fig 5.4: illustrate principle of printing

5.7.2Squeegee :- A flexible polyurethane blade (sometimes rubber) held in a rigid mount or handle

5.7.3.Ink**: -** Can take the form of a wide range of solids or dyes suspended in a fluid.

5.7.4.Substrate*:*-The base provides a surface for the substrate to be printed and the upper section secures the screen.

5.7.5.Machine base**: -** The base provides a surface for the substrate to be printed and the upper section secure the screen.

2.51.8 Squeegee system:

5.8.1.Double-blade squeegee:- In this system a parallel rubber- blade squeegees is driven across the screen with the print paste in the gap between them. Only the rear squeegee being raised slightly above it. When the next stroke is made, the leading squeegee for the first pass becomes the rear one for the reverse direction. The double-squeegee arrangement is simpler to construct than one utilizing a single squeegee that has to be lifted over the

pool of print paste at the end of each stroke, although this type is found in some modern semi-automated machines.

2.51.9 Magnetic – rod squeegee:-

This type is used in Zimmer flat – and rotary- screen printing machines except that the electromagnet is stationary. In a fully automatic flat- screen machines the rod rolls in the lengthwise direction and one passage is usually all that is required for adequate cover and uniformity. The diameter of the rod is usually small enough to allow print paste to flow over and around it at the end of a pass. It is clear that the screen distortion and wear are less where rolling rods rather than rubber-blade squeegees are used

Functions of squeegee

- In conventional screen – printing the squeegee carries two functions:
    - It deflects the stencil
    - Brings it into contact with the substrate
- The squeegee is held at an angle of typically 75 degrees to the horizontal.
- During the printing process the squeegee is moved across the stencil, creating a pressure wave in the ink.
- The actual point of flow is where the leading edge of the squeegee is in contact with the stencil. This is known as **"FLOW POINT"**[67],[76]

2.51.10 Advantages

1.larger repeats

2.multiple strokes for pile fabrics

2.51.11 Disadvantages

1.slow

2.no continuous patterns

Application of screen printing

Applications include: point of sale display and posters , gaskets ,watch dials, key pads, transfers, electronic circuits, car windscreen, road signs , architectural glass, tableware, nameplates, labels , ceramic tiles , vehicle instrumentation, mouse mats, office equipment, membrane switches , estate agents boards, textiles play cards etc.

2.52 Printing polymeric fibers

Pigment printing made it easier to print for polypropylene and polyester. Since its application is not limited to the fiber type. These fibers are hydrophobic in nature [78] Apart from pigments synthetic fibers can be printed well with dispersed dyes

100% polyester woven fabrics are usually printed with dispersed dyestuffs but there is a limited number of vat dyes that may be used to print these fabrics. Dispersed dyes give a broad scope of bright and deep shades .Only limited number of disperse dyes that can be applied on an unmodified (PETP).The wet fastness of these selected dyes is significantly reduced by excessive amount of non-ionic product. i. e. detergents, carriers, fixing accelerators, softening agents / antistatic agents. Cationic dyes are applicable to anionically modified polyester. With regard to this behavior, the printing paste is carefully formulated, depending on the dye and the fixation process used. It can also be printed by pigment inks which can be applied to any type of fibers without any obstacles. The most common paste used to print polyester is bases on low – solids thickener such as low – viscosity alginates or seed-flour derivatives. The auxiliaries of the thickener solution are defoamers and / printing oils and non- volatile acid donor .The acid donor that is frequently used is monosodium phosphate –to avoid chemical degradation in the alkaline medium of the thickener.

2.53 Chemical characteristics of dispersed dyes.

More than 50% of all dispersed dyes are azo compounds, about 25% are anthraquinones and the rest are methane, nitro and naphthoquinone dyes. These dyes are characterized by the absence of solubility groups and low molecular weight.

The dye fiber affinity is the result of different types of interactions:

- Hydrogen bond
- Dipole-dipole interactions
- Van der Waals forces[72]

2.54 Color fixation

There are three methods used to fix color on to printed polyester fabrics

1. Prolonged steaming i.e. 1 – 2 hours, at atmospheric pressure, using a carrier to course dyestuff migration.

2. Steaming for 20 – 30 minutes in a high pressure star –frame steamer using high temperature steam (1.4 – 2.0 kg/cm2; 20 – 28 lb/in2)[80]

3. Fixation by treatment for 30 – 90 second in dry heat (190 - 200°C) using a stenter or baking oven

The last two methods give the outstanding color yields. The first one makes use of the conventional equipment's

3 Experimental part

3.1 Materials

POP, PES plain weaved fabrics and POP non-woven fabric were used as material to be printed. The fabric thickness of each fabric was measured using Uni-Thickness-meter. The density of each fabric was calculated using the following eqn:

$$\rho = m/A \qquad (6.1)$$

Where - m is mass of the sample

A is total surface area of the sample

ρ is the density of the fabric

3.2 Chemicals

All chemicals used in printing were laboratory grade reagents Lambicol L491 conc (synthetic thickener): it is an oil dispersion of acrylic co-polymer partially neutralized for pigment printing. It is a cream (off-white) low viscous fluid with a pH range of 5.0 – 6.0. Ionic character: anionic /non-ionic

Neoprint LTA/E CONC. (Binder) it is a white color liquid with pH ranges from 8.5 – 9.5. It is an aqueous dispersion of vinylic resin, Ionic character: it is anionic-non- ionic.

Versa print red (pigment for printing) and other auxiliaries such as ammonia (pH balance) were used for printing respectively.

3.3 Preparation of printing material

The cloth which is to be printed must be free from oils fats ,starches and any impurities which can be done by desizing and then giving vigorous soaping to the material. If the material is dyed with some dischargeable color it must be ensured that it is free from acid.

3.4 Cleaning procedure

Samples were washed in Syntapon ;ABA 2g/l in cycles, 3times, liquor ratio 1:50.at 80˚Cfor 20mins .Between washing samples were rinsed alternatively with cold and warm water and then rinsed in distilled water at the same temperature and finally rinsed in cold distilled water.

3.5 Washing in dichloromethane

To make sure that our samples were clean enough they were then washed again in dichloromethane three times and then dried at room temperature. This procedure was conducted in the fume cupboard for safety reasons as the reagent used was volatile and having sharp smell, which can affect the respiratory system. After washing in dichloromethane they were sent to a spectrophotometer to check possible organic particles available on the surface of the fabric.

.

3.6 Thickness Measurements.

Fig:6.1. Instrument used to measure the thickness of fabrics.(UNI-THICKNESS-METER)

Test conditions

Pressure : 1kPa

Area of the plates : 1000mm^2

Under this test a fabric was put between two parallel spherical plates. At a given time interval the upper plate compresses the fabric and automatically gives the reading.

Table 6. 1:Details of the used fabrics

Fabric	Size (cm^2)	Density (g/m^2)	Thickness (mm)
100% Polyester	15 x 30	$1.06*10^{-2}$	0.46
100% Polypropylene	30 x 12	$9.12*10^{-3}$	0.45
Non – woven polypropylene	15 x 30	$4.93*10^{-3}$	0.68

3.7 Surface functionalization

3.7.1 Plasma parameters

- P [W], Plasma treatment depends on the power that is put into the discharge. The discharge current and the voltage determine the discharge power of the plasma source.

- P [W m $^{-3}$] The power density which is defined as the discharge power ρ divided by the discharge volume .

- L [W m $^{-2}$] The power loading which is defined as the discharge power ρ per exposed area of the sample surface .

- τ [s] The treatment time ,defined as the time of exposure to the plasma .In most cases the substrate is moving so that the treatment time is given by :

$$\tau = d/v_s \qquad (6.2)$$

Where d is the active length of the discharge in the direction of the substrate movement and v_s. is the substrate velocity.

- D[J m $^{-2}$] The energy dose onto the treated surface. D is defined as power loading L multiplied by the treatment time τ . (Is an important parameter to achieve desired surface properties)

$$D = L^* \tau \qquad (6.3)$$

3.8 *Procedure .*

Polyester and polypropylene fabrics were exposed to plasma – Diffusion Coplanar Surface Barrier Discharge. This device is appointed for treatment of plain materials with plasma at atmospheric pressure. It is possible to use different kinds of gases for plasma treatment. Plasma reactor contains following functional components: DSCBD plasma-chemical box,

DCSBD ceramic electrode Al2O3 (active area 9 x 20 cm2), HV power supply unit (500 watt,10-20 kHz, 15 kVp-p). The ceramic electrode is cooled by oil. Part of device is oil pressure pump and air cooler of oil

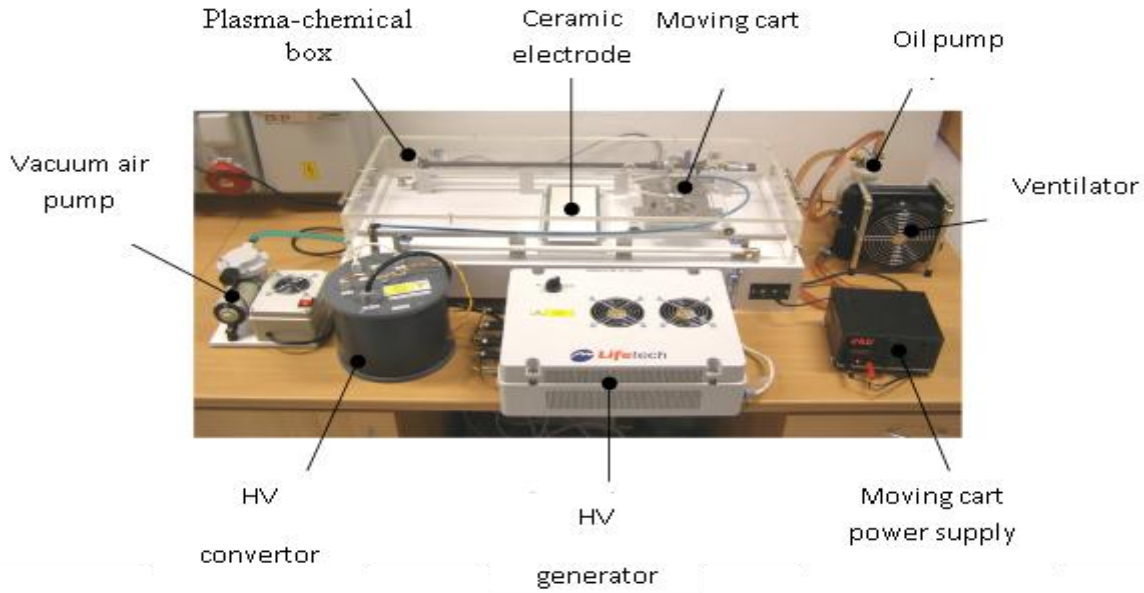


Fig 6.2 : Plasma-chemical reactor, model: DCSBD (Diffuse Coplanar Surface Barrier Discharge) A4-LIN

Treated samples were attached to movable trolley by means of vacuum sucker. Movable trolley is linked to linear displaced electrode. After inflammation of discharge on the surface of ceramic electrode movable trolley was initiated to work and fixed sample got into contact with plasma.

3.8.1 Percent weight loss after plasma treatment (ΔW)

The percent weight loss after plasma treatment of the fabric was calculated. The calculation method is given by the following equation:

$$\Delta W = [(W0 - W1)/W0] \times 100\% \qquad (6.3)$$

Where : ΔW is % weight loss

W0 is the original weight of the fabric

WI is the weight of the fabric after plasma treatment. [82]

X-RAY Photoelectron spectroscopy.

XPS is an analysis technique used to obtain chemical information about the surfaces solid material. It can be used to determine both composition of the sample in a non-destructive manner and the chemical information, such as binding constants, oxidation states and speciation. The sample under analysis is subjected to irradiation by high energy X-rays, which causes the K-shell electron to be ejected. [84].The ejected electron has a kinetic energy (KE) that is related to the energy of the incident beam (hv), the electron binding energy (BE), and the work function of the spectrometer (Φ)

$$BE = hv - KE - \Phi s \qquad (6.4)$$

Thus ,the binding energy of the electron can be calculated .

3.9 Hydrophilic measurement

3.9.1 Suction capacity test

Fig 6.3, experimental setting

3.9.2 Procedure.

Hydrophilicity of fabrics was evaluated by means of suction capacity test. A colored water solution was used as a test liquid for better visualization. Then the samples were immersed in the liquid at room temperature, 10mm below the liquid. First observations were done after 20 minutes, and the final one after 60 minutes.

3.10 Pigment printing

The term “pigment print” is used for any type of printed image that uses strictly pigments(synthetic organic material)The image of pigment printing is superior to that of any other method of printing ,including traditional silver –halide or metal-based.

A good quality pigment printing is characterized by brilliance and high color value relative to the pigment concentration in the paste, minimum stiffening in the handle of textile and generally acceptable fastness properties[83]

3.10.1 Preparation of printing paste

Apparatus used

- Plastic beaker
- Electric Stirrer
- Analytical balance

Chemicals used : (For stock paste)

- Lambicol L491-conc 14g/kg
- Neoprint (binder)LTAE – conc 150g/kg
- 26% Ammonia liquor pH = 9.5 (4 – 6kg)
- Water

Actual preparation

Printing paste was prepared and put in a sealed container (to avoid drying and contamination) a day before commencing printing so that it can stand overnight. Pigment was added over stock solution and homogenized with the aid of electric stirrer for some time to make the paste.

3.10.2 Printing technique

Printing was carried out using Flatbed (screen) printing machine, Type Zimmer-Johannes mini- MDF/752.

Fig 6.4: Zimmer – Johannes mini- MDF/752

3.10.3 Procedure

The fabric samples were put on a flatbed machine with the plain screen on the fabric .Print paste was put on one side of the screen and applied with the help of steel rod .Steel rod moved with the help of electromagnetic assembly and applied the paste on the fabric .The fabric was then dried in a drying oven at 80°C for 5minutes. It was then cured at 150ºC PES and 120ºC POP. Afterwards different tests procedures were carried out on a fabric.

3.10.4 Rubbing fastness

Fastness to rubbing measures how much of the color present in your product will be transferred when exposed to a certain amount of rubbing against a given material. The rubbing is tested dry or wet in wet rubbing we wet the rubbing cloth according to test method and give rating by comparing the staining with the gray scale .Similarly for dry rubbing we check the rubbing with dry rubbing cloth and compare the staining with gray scale for ratings.

Color fastness is the main test which is always required for every colored fabric either it is printed or dyed. If the color fastness is good then other properties like washing fastness and durability etc. improves automatically, because the rubbing is a method to check the fixation of the color on the fabric. So if fixation is good it's washing properties will be good.[85][86]

Rubbing fastness depends on:

- Nature of the color.
- Depth of the shade
- Construction of the fabric.

Nature of the color: - Each colors either it is pigment, reactive, disperses or direct has its own fastness properties to rubbing.

Results that can be achieved in Normal Conditions are:

	Dark Shade	Medium Shade	Light Shades
Dry	3-4	4	4 – 5
Wet	2 – 2.5	3	3.5 - 5

This test method was carried out following international standard (AATCC-08)

3.11 Equipment used for measurements

1. Stain Meter. 2. Cotton Rubbing Cotton. 3. Grey Scale. 4. Color Matching Cabinet.

Size of fabric

Cotton fabric used for this test was cut into pieces of 5cm x 5cm.

3.12 Procedure

- The test specimen was locked onto the base of the stain meter.
- With the aid of spinal clip a 5cm x 5cm of the white cotton fabric was set to the finger of the crock meter.
- The covered finger was lowered onto the test sample
- Hand crank was turned at a rate of the one turn per second.
- After ten cycles, the white rubbing test cloth was removed and evaluated with the grey scale.

3.13 Color yield

A colorimetric spectrophotometer uses a light source to light the specimen being measured. The light reflected by the object then passes to a grating which breaks it into the spectrum. The spectrum falls onto a diode array which measures the amount of light at each wavelength. This spectral data is then sent to the processor where it is multiplied together with data table values for the selected CIE illuminant and 2 and 10 standard observer functions to obtain the XYZ values.[87][88]

In principle, any instrument used for color measurement includes the following main components

- Illumination device
- Monochromator (or wide – band filter)
- Sample holder
- Radiation –measuring device

Color measurement start with the reflection values for the color sample.

3.14 Technical parameters

Instrument : Data color international SF600

Band pass : 10nm

Visible range : 400 – 700nm

Power requirements 85 – 264 VAC

47 – 63 Hz

80 VA peak

35VA typical

Absolute operation range 5 to 40^0C, 5% - 85% non-condensing relative humidity.

3.15 Procedure:

The instrument was calibrated with a black standard (hollow light trap) for the zero and a white standard for maximum reflectance.

The reflectance values of the printed fabrics were measured using spectrophotometer data color international (SF600) under illuminant D65 .The fabric was measured three times and measurements were taken from both sides i.e. back and front side. Color strength expressed as K/S value ranging from 400 to 700nm with 10nm interval within the visible spectrum was calculated using Kubelka –Munk equation. The color intensity increases with increasing K/S (sum) value.

$$K/S = (1-R)^2/2R \quad (6.5)$$

Where K = absorption coefficient, depending on the concentration of colorant

S = scattering coefficient, caused by the dyed substrate.

R = reflectance of the colored sample.

3.16 Scanning Electron Microscope (SEM).

Backgroung.

The SEM is a microscope that uses electron rather than light to form an image.

The advantages of the SEM is it's high resolution (down to 1nm in modern instruments). Intuitive image interpretation. Minimal sample preparation. High analysis throughput and Relatively low setup cost.

The main components of a typical SEM are electron column, scanning system, detector ,display ,vacuum system and electronic control[87]

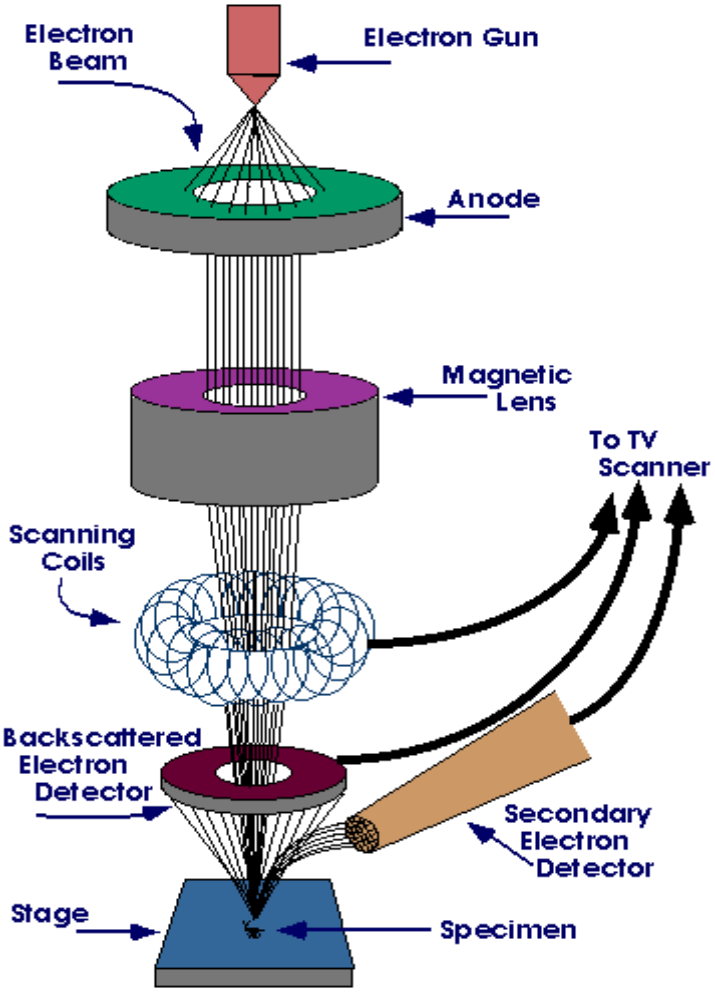


Fig6.6: Schematic diagram showing the essential components of scanning electron microscope.

3.17 How does it work

In this type of microscopy electrons do not penetrate the sample .Instead the sample is coated with gold which causes the electrons to bounce off the surface of the sample The electron beam is scanned in a back and forth motion parallel to the sample surface . A detector captures the electrons that have bounced off the surface and the pattern of deflection is used to assemble a three dimensional image of the surface.

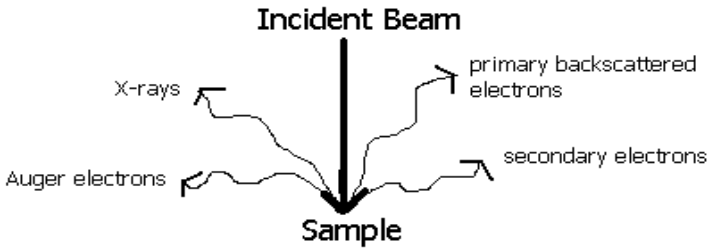


Fig6.7 : Shows interaction of the incident beam with the substrate

3.18 Sample preparation

Since the SEM uses electron to produce an image, most conventional SEM's require that the sample be electrically conductive. Other materials such as metals are conductive therefore need not to be prepared for SEM. In order to view nonconductive samples such as plastics, we must cover the sample with a thin layer of a conductive material. This is done with the aid of a device called sputter coater.

Fig6.8: sputter coater

The sputter coater uses argon gas and a small electric field. The sample is placed in a small chamber which is at vacuum. Argon gas is then introduced and an electric field is used to cause an electron to be removed from the argon atoms to make the atoms ions with positive charge. The Ar ions are then attracted to a negatively charged piece of gold foil. These gold atoms now settle onto the surface of the sample, producing a gold coating.

Precaution

If the chamber is not at vacuum before the sample is coated, gas molecules' gets in the way of argon and gold. This could lead to uneven coating or no coating at all.

Instrument setting

SESM MAG 1.5 kx

HV 30.0KV

DET BE Detector

Fig6.9 :TS5130SEM Detector of Vega Tescan

3.19 Procedure.

The surface morphology of the fabric after plasma treatment was investigated by SEM, (TS 5130 SEM Detector product of Vega Tescan). Specimens were mounted and gold sputtered to give the samples electronic conductivity under vacuum prior to observation.

3.20 Optical Microscope.

Fig:6.10: Optical microscope

It is often referred to as light microscope because it uses visible light to produce a magnified image. It is a sophisticated instrument capable of providing images with a resolution of the order of 1μm, molecular information via birefringence, chemical information, color changes, through the use of specific dyes. It can be used in reflected as well as transmitted modes. It is a powerful technique, particularly for specimens that transmit in a visible region of spectrum.

Problem with any light microscope is, a user must select the right magnification, contrast, resolution and focal plane all at the same time. However, mainly light microscopes are equipped with specialized optics that enhances contrast so that any specimen placed on it can be captured.

N.B: The specimen must be thinner to allow light to pass through .Thicker specimen would give a blurred image.

Fig 6.11:Microtome and steel knife,used to cut the sample

Procedure

- The substrate was first treated with fixative, Duvilax KA-11(glue) and Spolion 8 (detergent)and dried overnight at room temperature followed by treatment with glue only .
- The substrate was then embedded in a wax.
- After cooling, the wax – embedded substrate was cut to 50 microns using microtome and steel knife.
- The substrate was put on a slide and a special liquid was poured on it
- It was then taken to the microscope for observations

4 Results

4.1 Plasma effect

We used surface treatment in order to produce special functional groups at the surface of fabrics, so that there would be special interactions with other functional groups and hence to increase surface energy. To verify the chemical changes underwent on the surface of our fabrics, XPS resolution spectra for both untreated and treated were taken. It can be seen from survey spectrum in fig 7.1 that there are two peaks at 284.00 and 532.00 all assigned to C 1s for the untreated PP fabric .For the treated PP (Fig. (b)) four new peaks appeared at 284.58 eV for C 1s,534,58 for O 1s,408.57Ev for N 1s, and 200.08 eV for C1 2p respectively . From the results obtained it was seen that plasma treatment activated the surface of materials to become polar, to improve wet ability and adhesion properties (as figure a, b, c are revealing the effect). If the surface could be modified to be more polar the printing and finishing procedures could be improve and refined.

7.1.1. Results

XPS- results for POP untreated & treated fabrics.

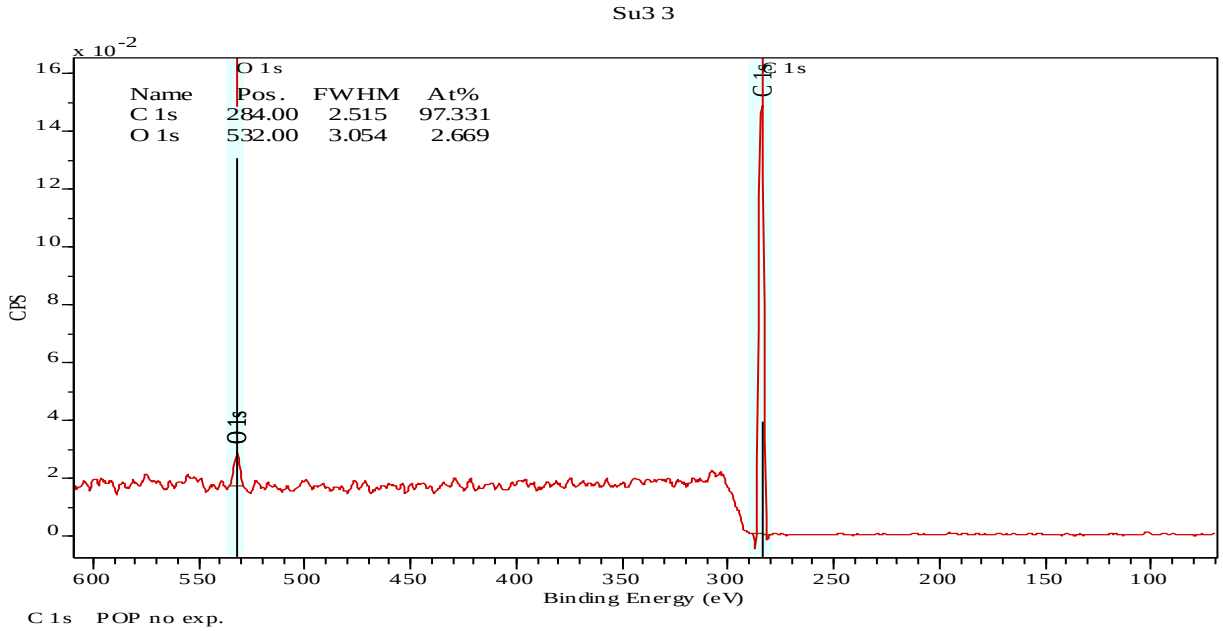


fig 7.1(a). XPS results for untreated POP.

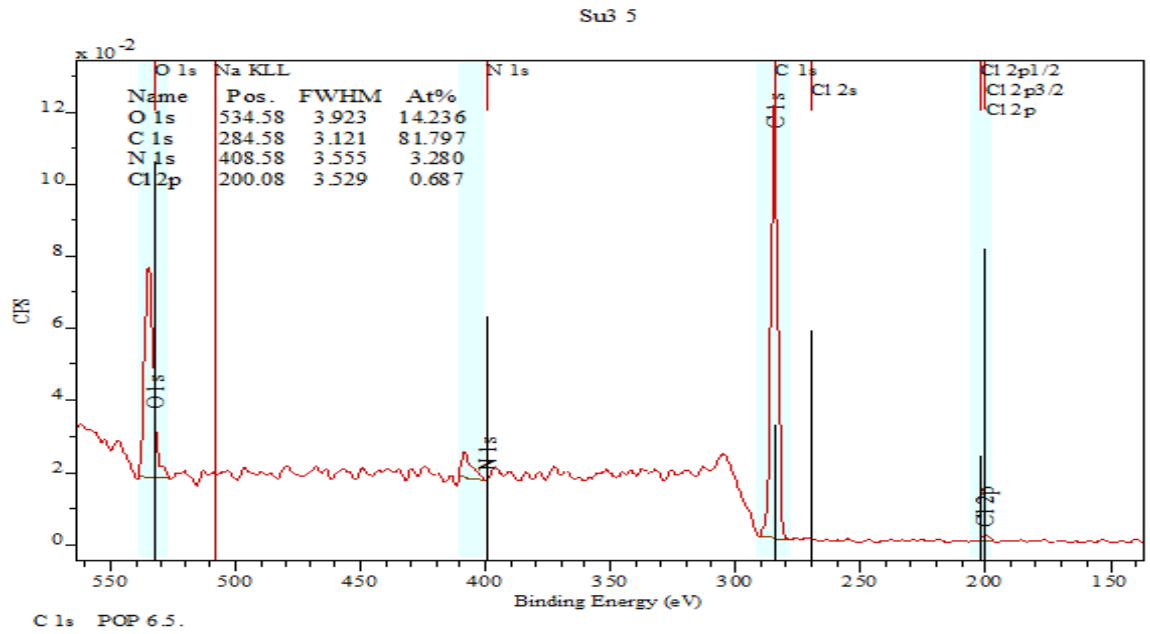


Fig 7.1 (b) XPS results for the treated POP

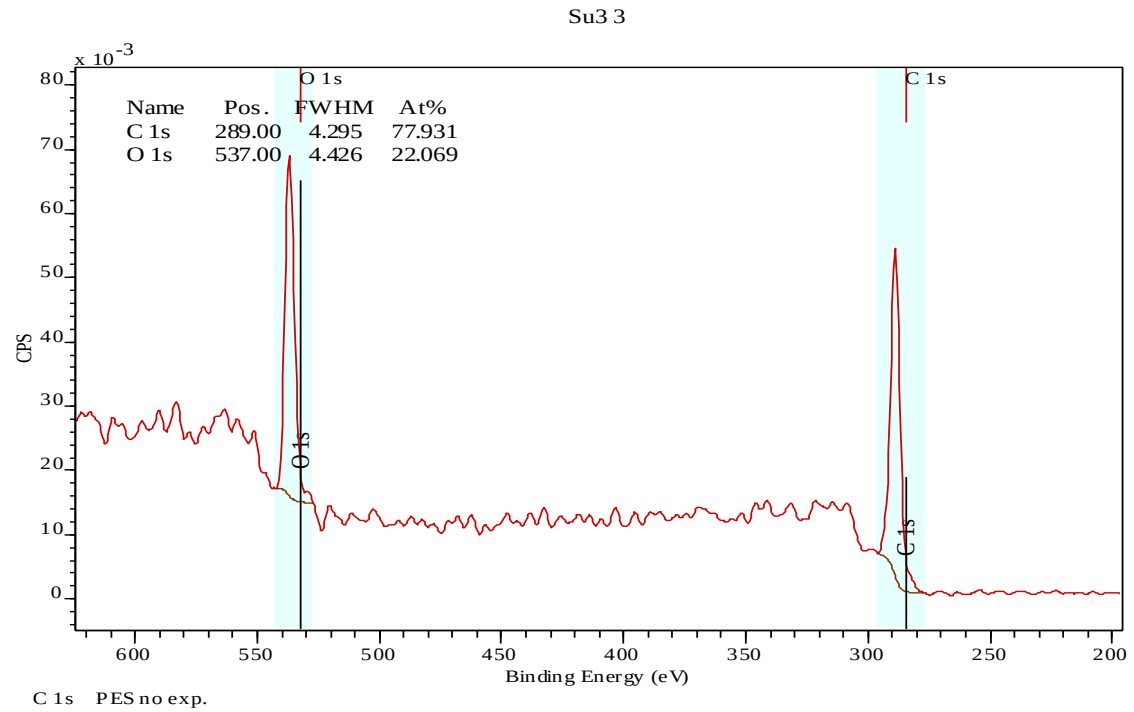


Fig7.2: (a)XPS results for untreated PES

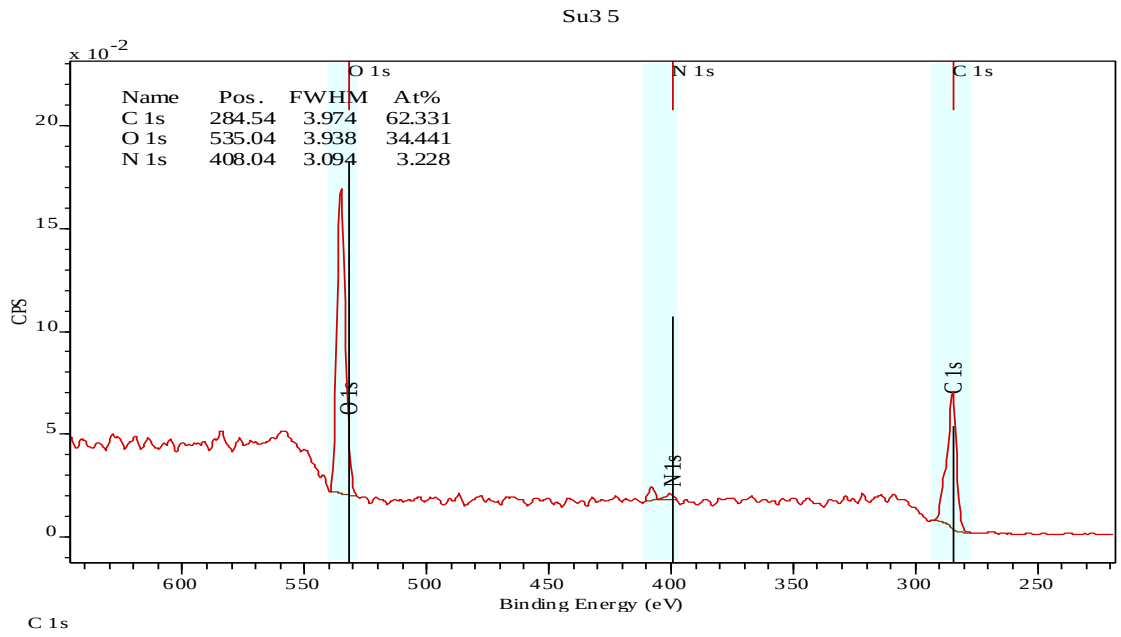


Fig7.1 (b)XPS results for treated PES.

4.2 Mechanical properties

4.2.1 Percent weight loss

From the results obtained I can generally say there is no much loss in weight of fabrics after plasma treatment but in comparison between the three fabrics, polyester shows higher loss than polypropylene fabrics.(both the nonwoven and the woven fabric)

4.3 Surface functionalization

4.3.1 Suction capacity test

The material sucked very unevenly and all the tested sample suction stopped, when ¼ to more or less ¾ of the surface of the fabrics were saturated. The plasma treatment quickly increases the wet ability of textile fabrics in the shortest time (20minutes) at the longest length of 190mm for PET, at relatively the same time WPOP obtain 117mm for WPOP and 39mm for MWNPOP after 50minutes. For the best effect of hydrophilicity achievement it is necessary to treat different substrates for different time. The nonwoven fabric needed for maximum rate of modification the time of 10s. The woven fabrics needed maximum time of 30s.

Meaning then that the process for the woven textile fabric is longer than the nonwoven fabric. Polyester was a fast absorbing of them all. The reasons are based on specific surface of single fibers and the orientation of those single fibers on the textile fabric. As we know

that woven fabrics are produced by interlacing the fibers which give them more strength, in nonwovens there is no interlacing of fibers. The other reason lies on the functional groups anchored by plasma treatment, and the energy each substrate receive from the treatment. The particles of the plasma are deactivated after contact with the surface of fiber and only a small amount of particles can penetrate the fiber. For achievement of the comparable effect with woven fabrics it is necessary to enhance the time of modification, which was experimentally proven

7.3.1.1.Results

Influence of plasma treatment time on suction capacity

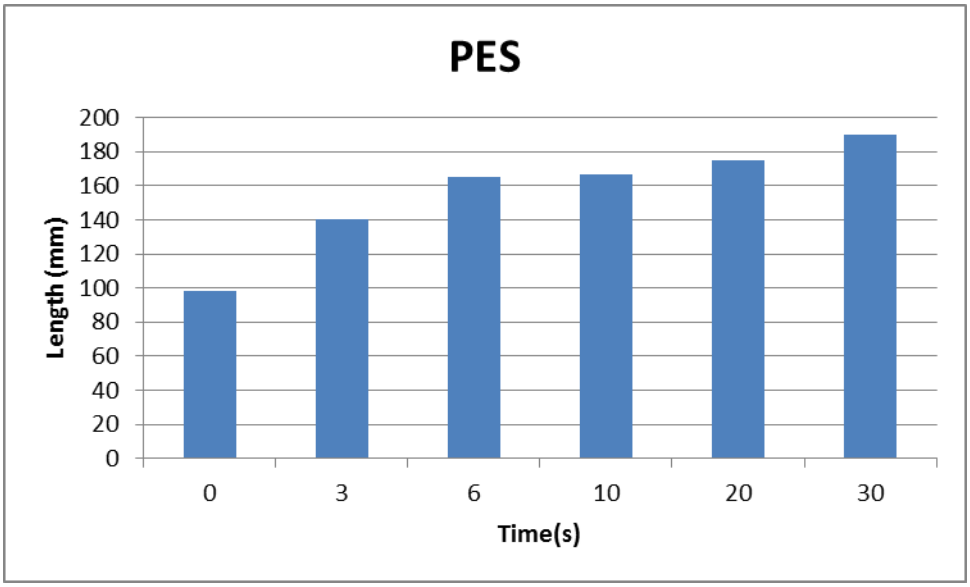


Fig 6.15: (a) polyster fabric

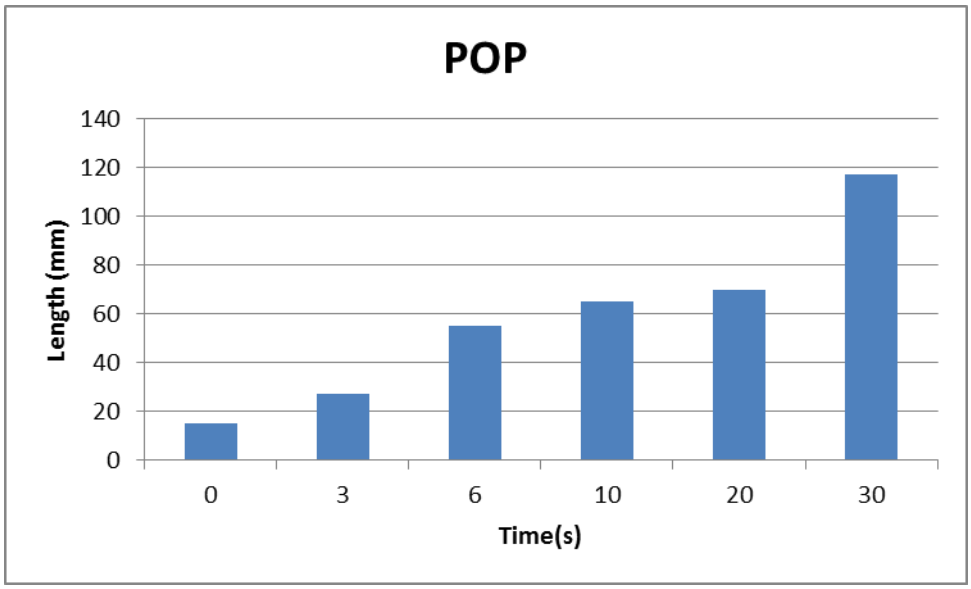


Fig 6.15: (b) polypropylene fabric

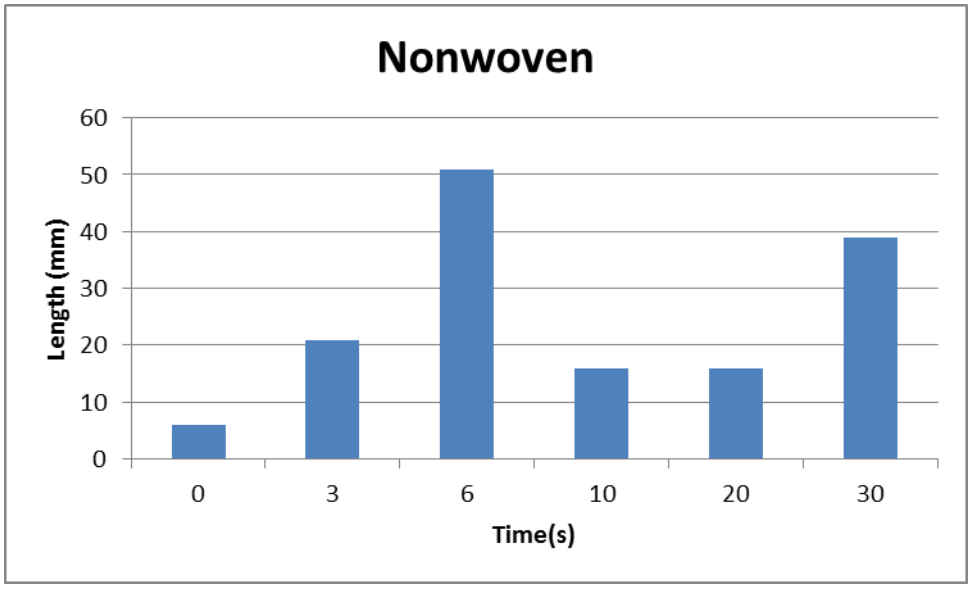


Fig 6.15: (c)nonwoven polypropylene

4.4 Printing

4.4.1 Discussion

A small decrease in the viscosity of the print paste was observed by the addition of binder however, the rubbing fastness of the print paste was improved because cross linking of the binders was done with the fabrics.

7.5. Color fastness.

Technical parameters

Instrument : AT Color

Illumination : D 65

Source : grey scale (for both original and the sample)

Range : 1 – 5

7.5.1. Procedure:

At this stage we compare the contrast between the treated and untreated white rubbing cloth with grey scale, rated 1 to 5.

After printing, drying and curing, materials were subjected to the test conditions. The extent of staining was assessed by placing a sample of the unstained materials alongside the stained material. Then a judgment of the degree of contrast between the two was then made by comparing with the relevant steps in the grey scale under recommended conditions of illumination.

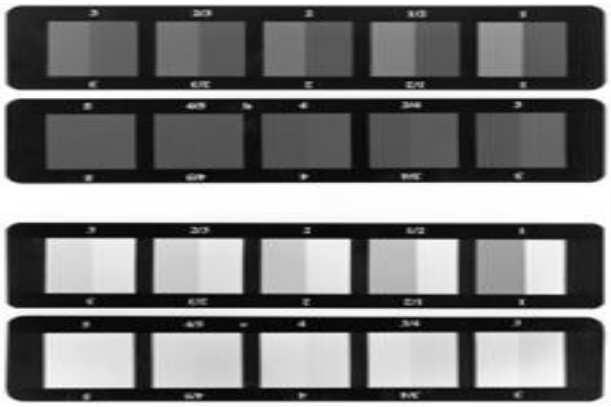


Fig7.2: Grey scales(top) the scale used to assess the color change of a sample , (bottom) the scale used to assess attaining

7.5.1.1 Discussion

Results obtained from this test were generally rated between good to excellent without any remarkable changes between the treated and non-treated fabrics. This fact is due to the binding system used in printing paste preparation. Binders have direct effect on

colorfastness of the material. The higher the cross-linking action done by the binder the stronger the paste is glued on a fabric and little staining effect.

Table:7.2 (a): Grey Scale results, PES 30g/L

Sample		100% binder		75% binder		50% binder	
		Dry	Wet	Dry	Wet	Dry	Wet
Untreated	Staining	4	4-5	2-3	3-4	3-4	4-5
	Color change	3	2	3-4	3	2-3	3-4
3s	Staining	4	4-5	2-3	4	3-4	3
	Color change	3-4	3-4	3-4	3-4	2-3	3-4
6s	Staining	4	4-5	2-3	3-4	3-4	3-4
	Color change	3-4	4-5	3-4	3-4	3	3
10s	Staining	4	5	3	3-4	4	4
	Color change	5	4	3-4	4	3-4	3
20s	Staining	3-4	5	3	4	3-4	3-4
	Color change	4-5	4	3	5	3-4	4-5
30s	Staining	4	5	3-4	4	4	4-5
	Color change	4	4	3-4	3-4	3-4	3-4

Table 7.2 (b) :Grey Scale, PES 15g/L

sample		100% binder		75% binder		50% binder	
		Dry	Wet	Dry	Wet	Dry	Wet
Untreated	Staining	4	5	4	4	2	4
	Color change	4	4	4	3	3	4
3s	Staining	4	5	4	5	3	4
	Color change	4	5	4	4	3-4	4
6s	Staining	4	5	4	5	3	5
	Color change	4-5	4-5	4	3-4	4-5	4
10s	Staining	4	4-5	4	4	4	4
	Color change	4-5	5	3-4	4-5	4	5
20s	Staining	5	5	4	4-5	4	5
	Color change	4-5	5	4	4-5	4-5	5
30s	Staining	5	5	4-5	5	4	5
	Color change	4	4-5	4	4	4	5

Table: 7.3 (a)Grey Scale results, Woven POP 30g/L

Sample		100% binder		75% binder		50% binder	
		Dry	Wet	Dry	Wet	Dry	Wet
Untreated	Staining	4	3-4	3-4	2-3	3-4	2
	Color change	3	2-3	3-4	3	4	3
3s	Staining	4	3	3-4	2-3	4	2
	Color change	3-4	3	3-4	3	3-4	2-3
6s	Staining	3-4	3-4	3-4	2-3	4	2-3
	Color change	3	3	3	3	3-4	2-3
10s	Staining	3-4	3-4	4-5	2-3	4	2-3
	Color change	4	3	4	3	3	4
20s	Staining	3-4	3	4	3-4	3-4	2-3
	Color change	3-4	3-4	3-4	3	3	3
30s	Staining	3-4	3-4	4-5	3-4	3-4	3
	Color change	3	3	3-4	3	3	2-3

Table : 7.3 (b) Grey scale results ,Woven Polypropylene 15g/L

Sample		100% binder		75% binder		50% binder	
		Dry	Wet	Dry	Wet	Dry	Wet
Untreated	Staining	4-5	3	4-5	3	4-5	3-4
	Color change	3-4	3	4	3-4	3	3
3s	Staining	4-5	3	3-4	3-4	4-5	3-4
	Color change	3-4	3	3-4	3-4	3-4	3
6s	Staining	4-5	3	4-5	4	4	3-4
	Color change	3-4	3	4	4	3-4	3
10s	Staining	3-4	3	4-5	4	3-4	3-4
	Color change	4	3	4-5	4-5	3-4	3-4
20s	Staining	3	3	4-5	4	4	3
	Color change	3-4	3	4-5	4-5	3-4	3
30s	Staining	3	3	4-5	4	4	3-4
	Color change	3	3	4-5	4-5	3-4	3

Table 7.4 grey Scale results, Non-woven POP fabric 30g/L

Sample		100% binder		75% binder		50% binder	
		Dry	Wet	Dry	Wet	Dry	Wet
Untreated	Staining	4	3	3-4	2	2-3	2
	Color change	4	3	4-5	3-4	4	3
3s	Staining	4	3	3-4	2	3	3
	Color change	5	4	3	3	3	2-3
6s	Staining	4	3	3	2-3	3	2
	Color change	3	3	3-4	4	3	2-3
10s	Staining	3	3	2-3	2	2-3	2
	Color change	3	3	3-4	2-3	3	3
20s	Staining	3-4	3	2-3	2	3	2-3
	Color change	3	3	3-4	4	3-4	3-4
30s	Staining	4	3	3-4	2	2-3	2-3
	Color change	4	4	2-3	2-3	3-4	3-4

4.5 Color yield

4.5.1 Discussion

The results obtained from the spectrophotometer showed that for a non-woven POP fabric an increase in wet ability was achieved but at a relatively low intensity of plasma treatment. Once the optimum intensity was reached, a sharp drop in wet ability was obtained provided the plasma treatment intensity was further raised. On the other hand it showed better results at reduced binder content at the same concentration of pigment. This means that a choice of a binder, has an effect on color strength of textile fabrics. For POP fabrics results were enhanced by plasma intensity. For PES the back side showed more revealing results than the front side, the pigment paste might have penetrated more deeply into the structure rather than forming film on top. This may be due to the topographic effects caused by plasma and its geometric structure as we already know that it is not very crystalline as compared to POP. It was also proven in this work that PES looses more weight after plasma treatment in comparism with polypropylene, although in that case there was no significant loss. The differences are stipulated in the figures below.

7.5.2. Results

Spectrophotometry graphs for woven polypropylene

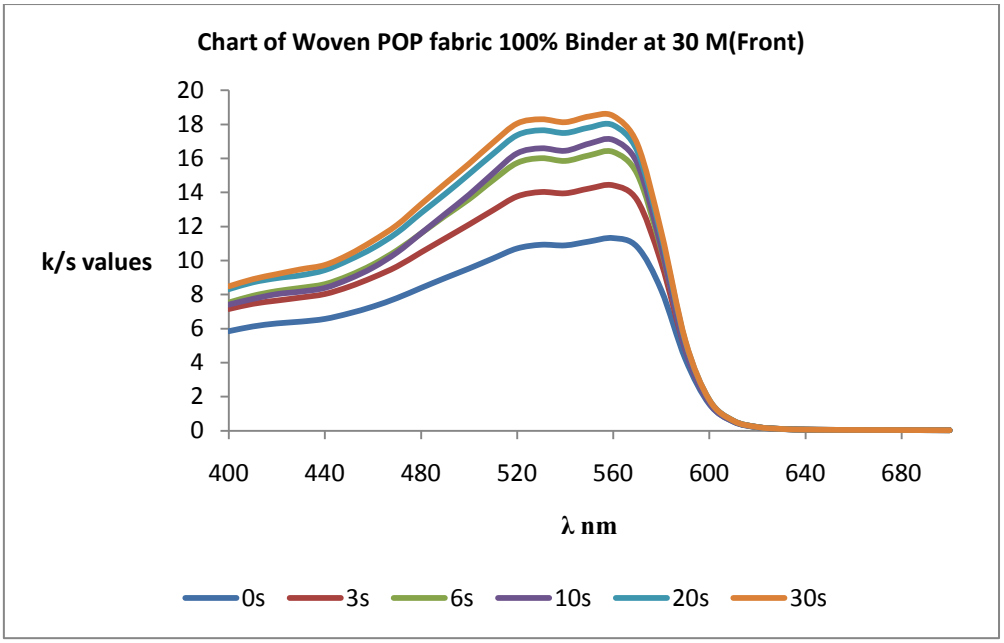


Fig:7.1.(a) woven polypropyle fabric 100% binder at 30M; front side

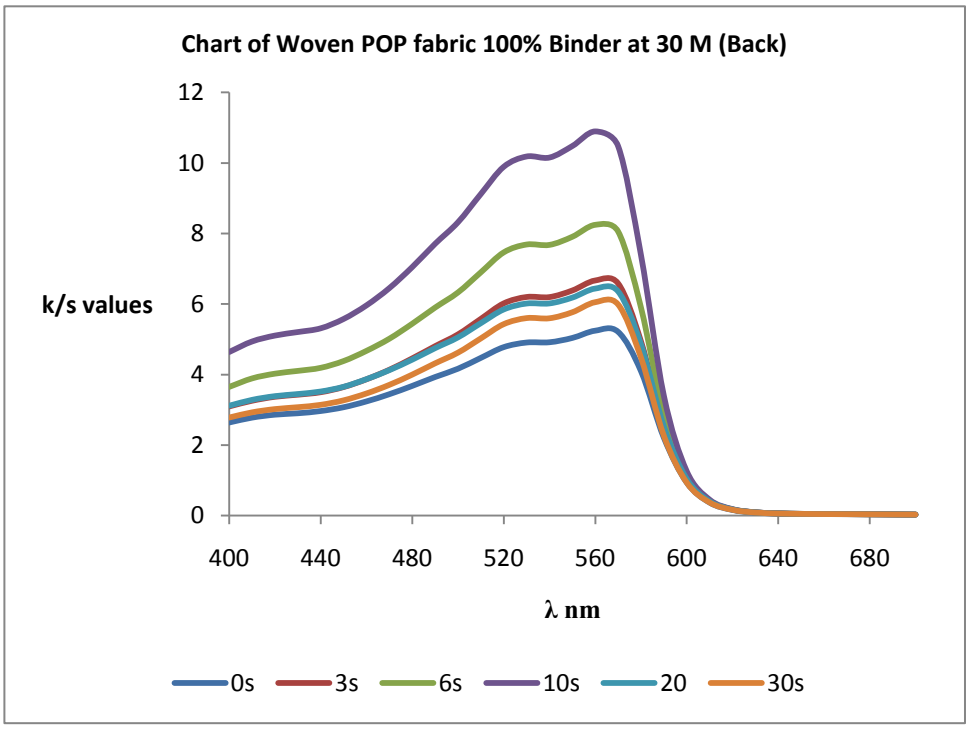


Fig : 7.1 (b) woven polypropylenefabric 100% binder 30M; back side

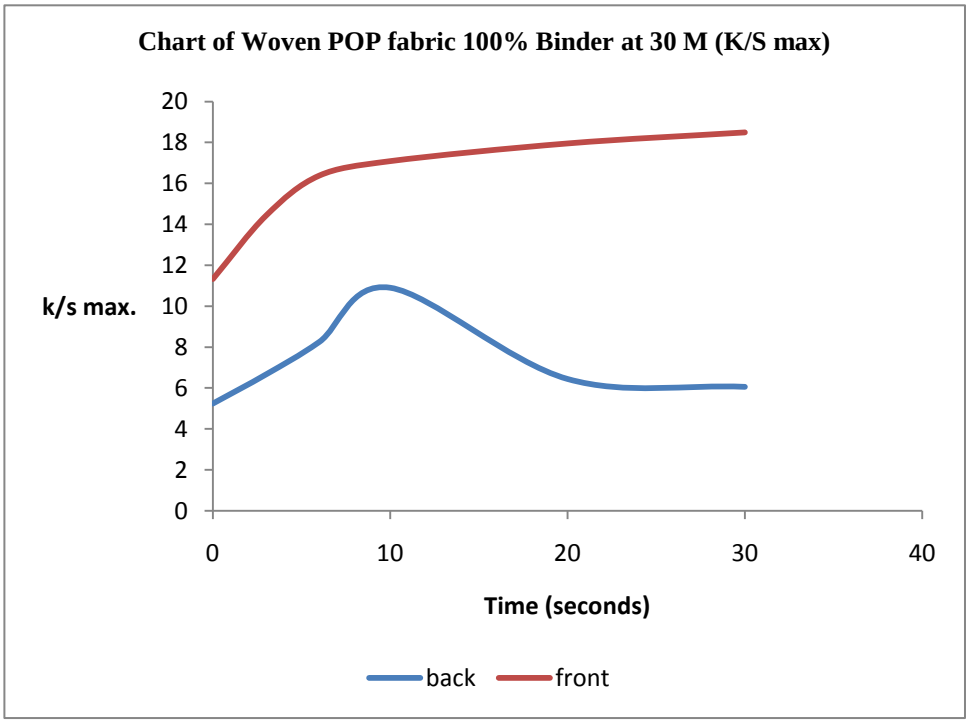


Fig 7.1(c) woven polypropylene fabric 100% binder 30M; k/s maximum

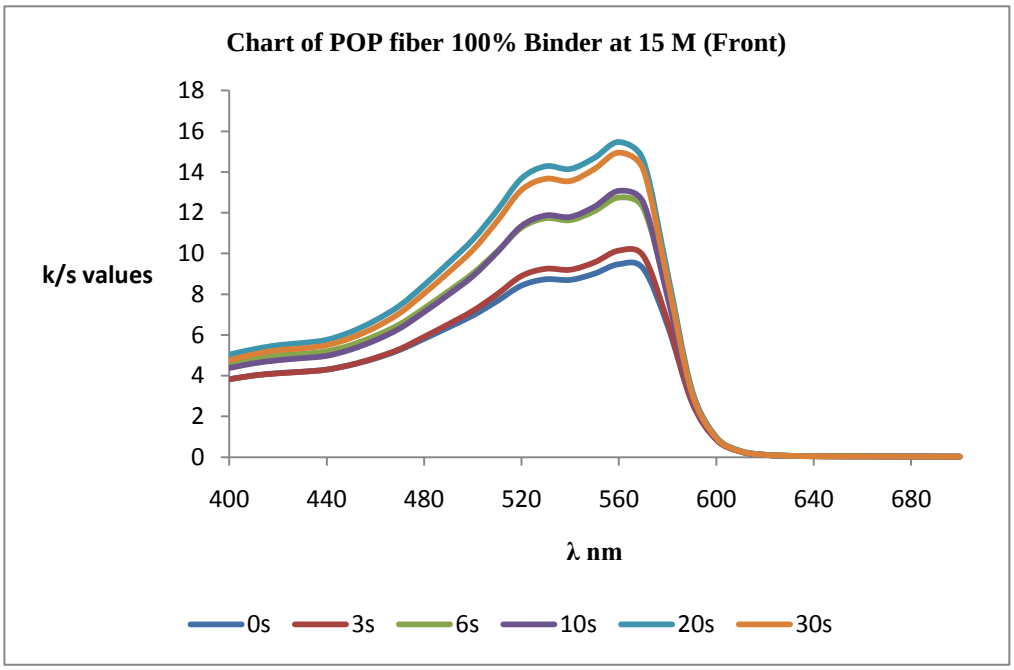


Fig:7.1.1.(a) woven polypropylene fabric 100% binder, 15M; front side

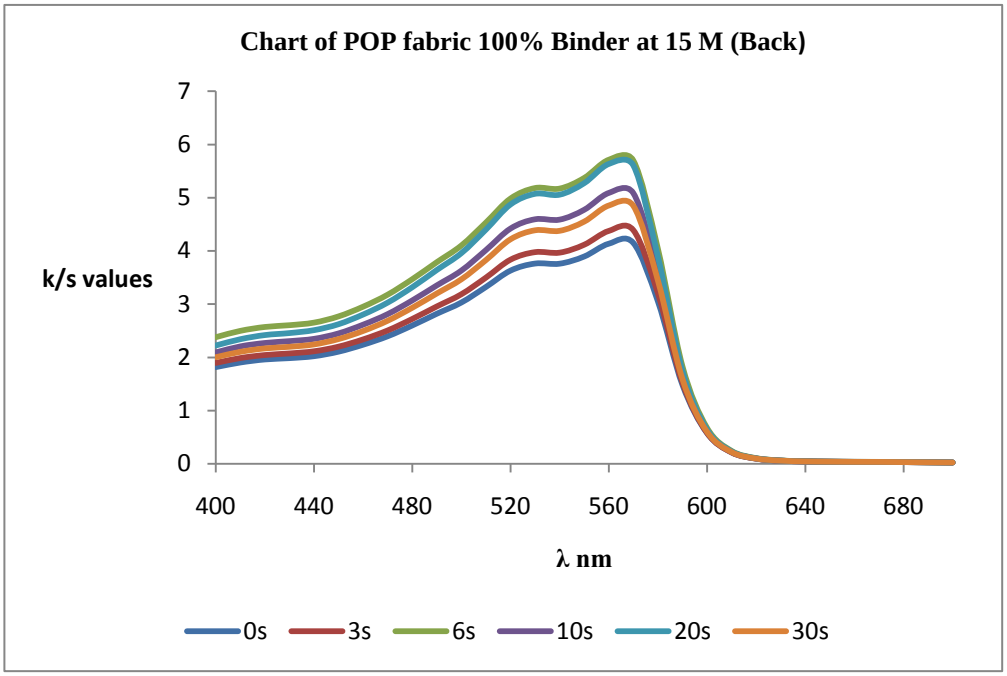


Fig: 7.1.2(b) woven polypropylene fabric 100% binder,15M;back side

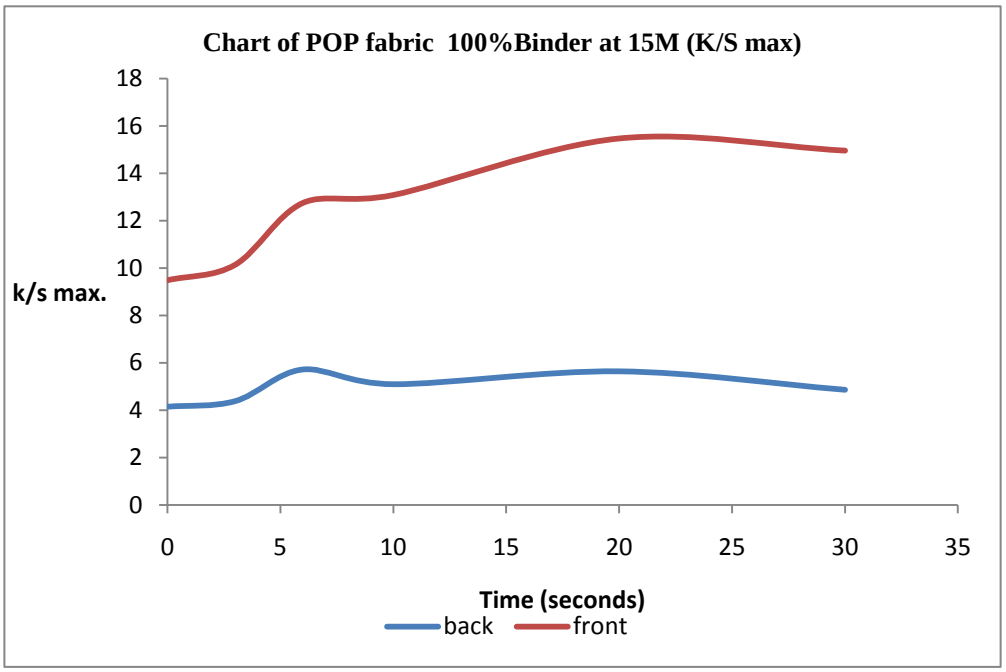


Fig: 7.1.3 (c) woven polypropylene fabric 100% binder,15M k/s maximum

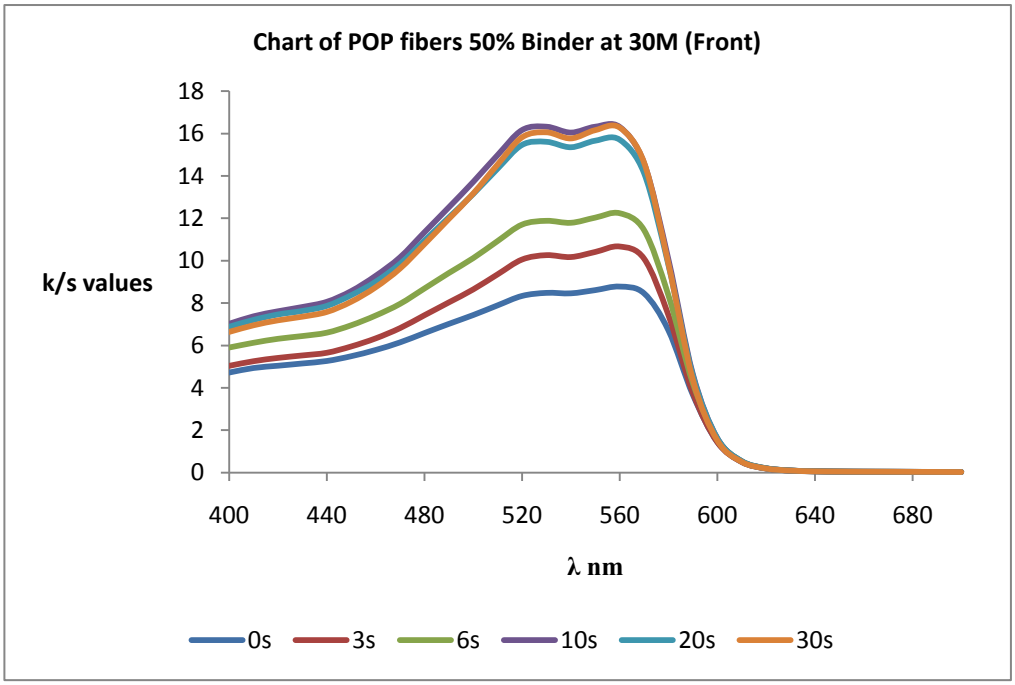


Fig 7.2 (a)woven polypropylene fabric ,50% binder,30M; front side

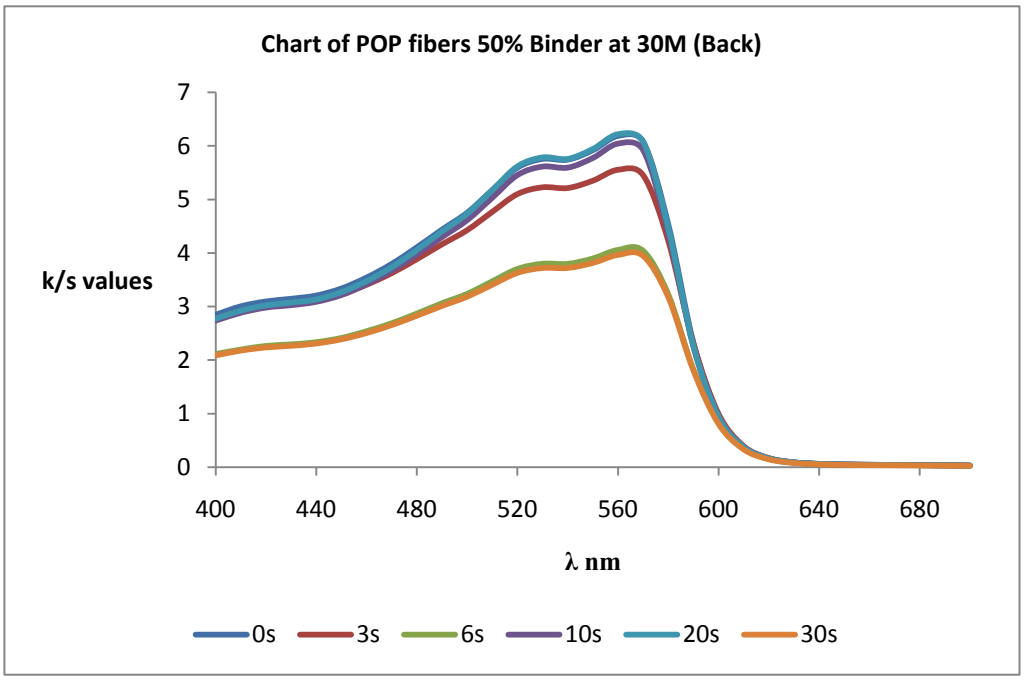


Fig: 7.2 (b) woven polypropylene fabric ,50% binder ,30M; back side

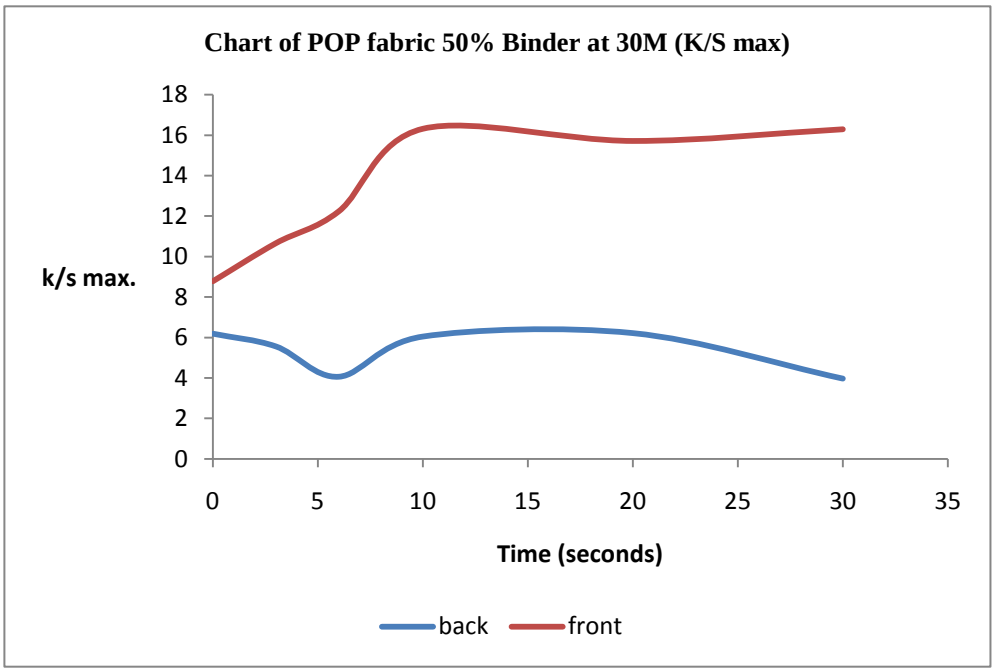


Fig 7.2 (c) woven polypropylene fabric ,50% binder ;30M ;k/s maximum

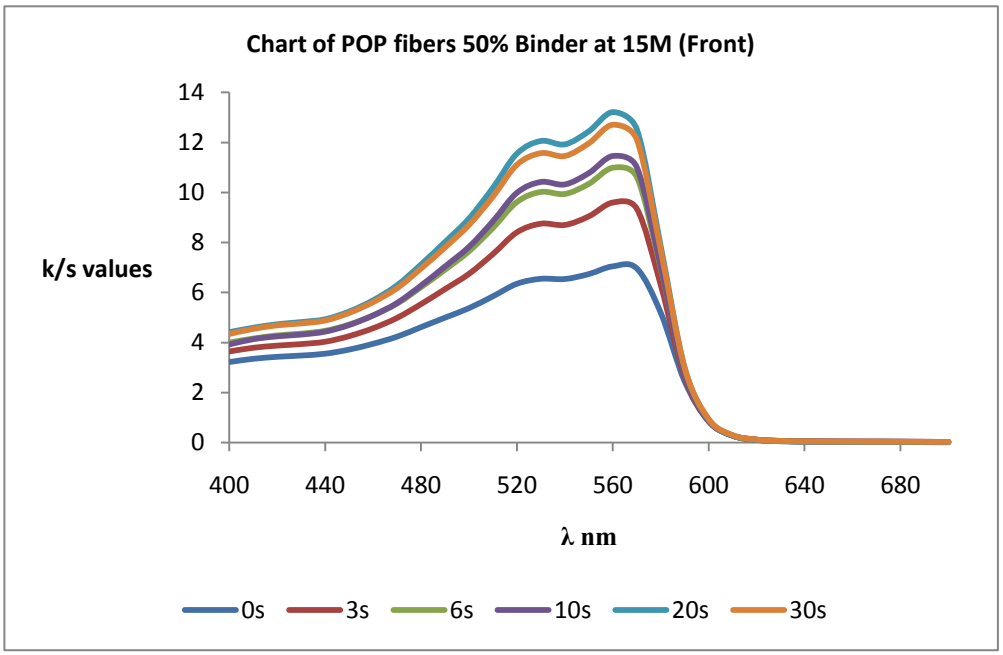


Fig: 7.2.1. (a) woven polypropylene fabric, 50% binder, 15M ;front side

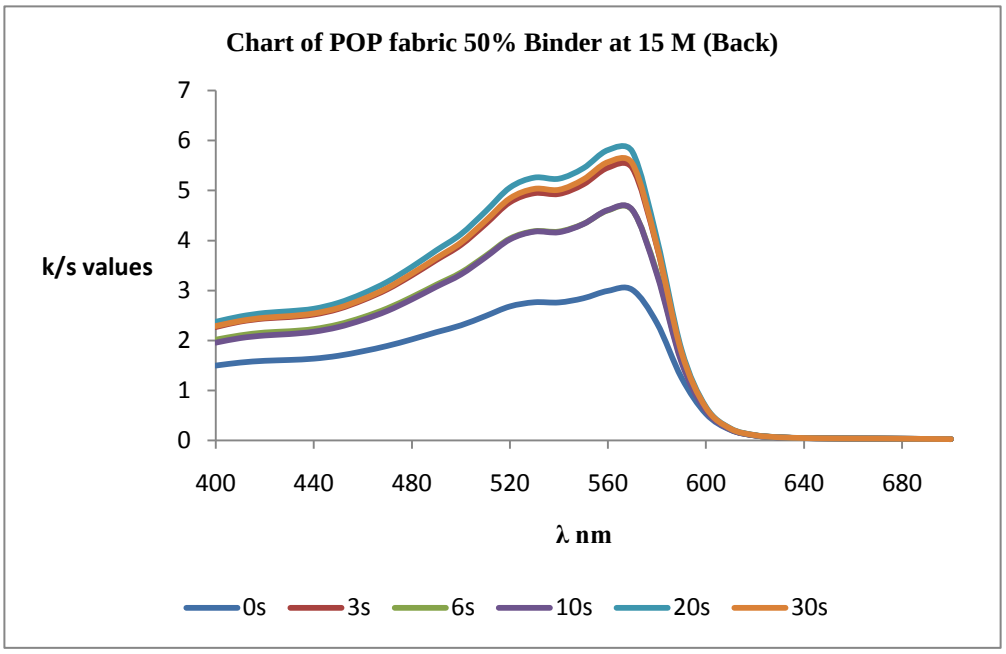


Fig 7.2.2:(b) woven polypropylene fabric ,50% binder,15M ; back side

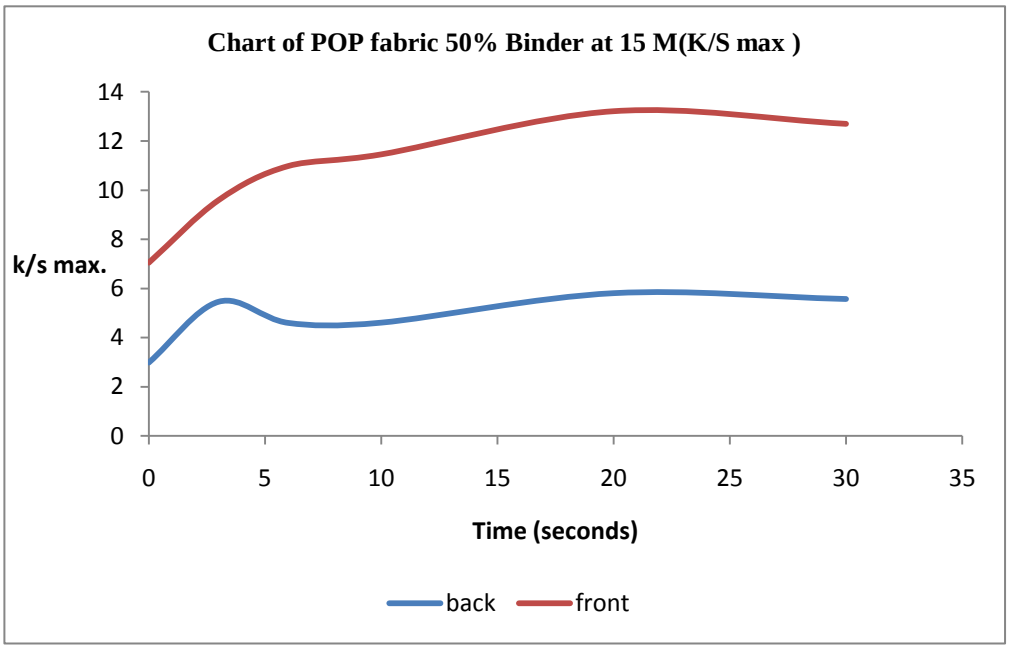


Fig 7.2.3:(c) wovenpolypropylene fabric ,50%binder,15M; backs ide.

Spectrophotometry graphs for polyester

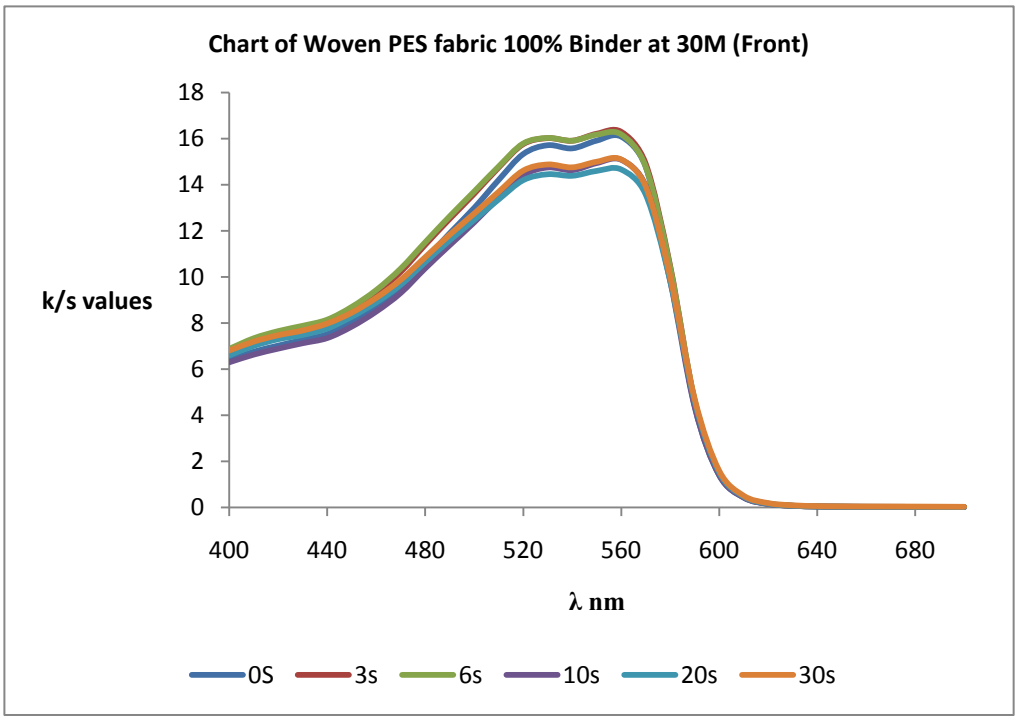


Fig 7.3:(a) woven polyester fabric ,100% binder,30M front side

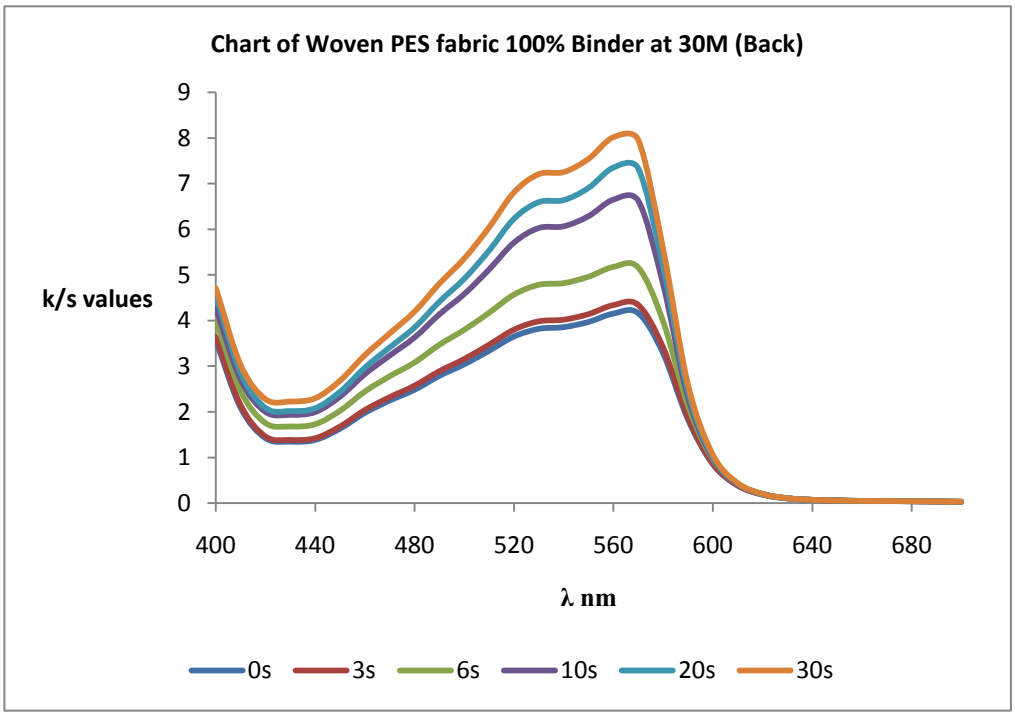


Fig 7.3:(b) woven polyester fabric ,100% binder , 30M ; back side

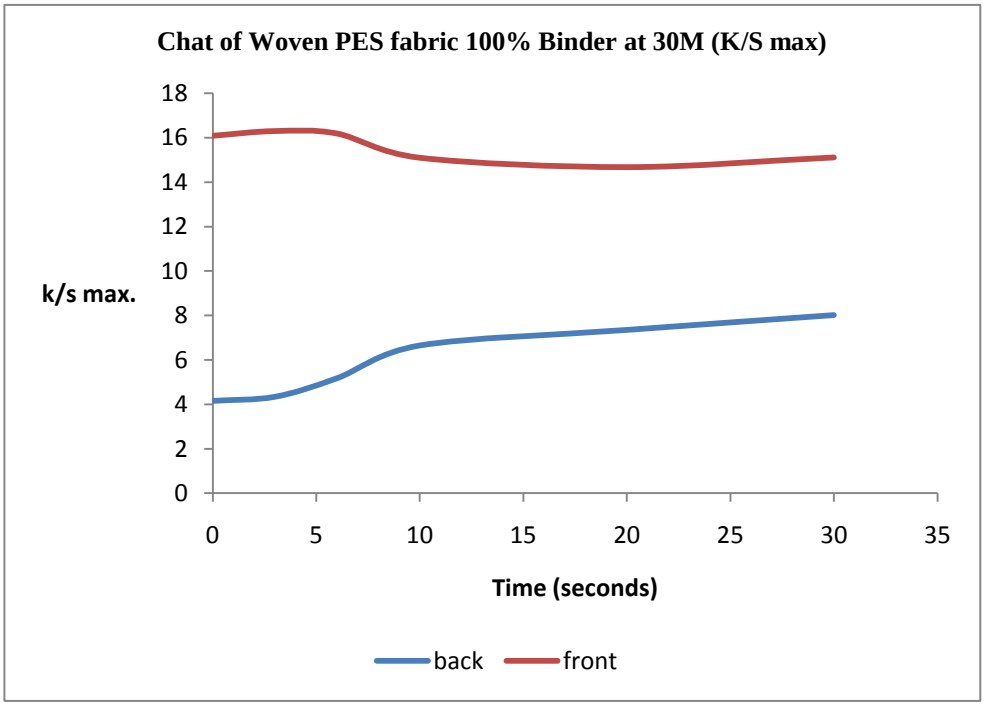


Fig 7.3:(c) woven polyester fabric ,100% binder ,30M k/smaximum

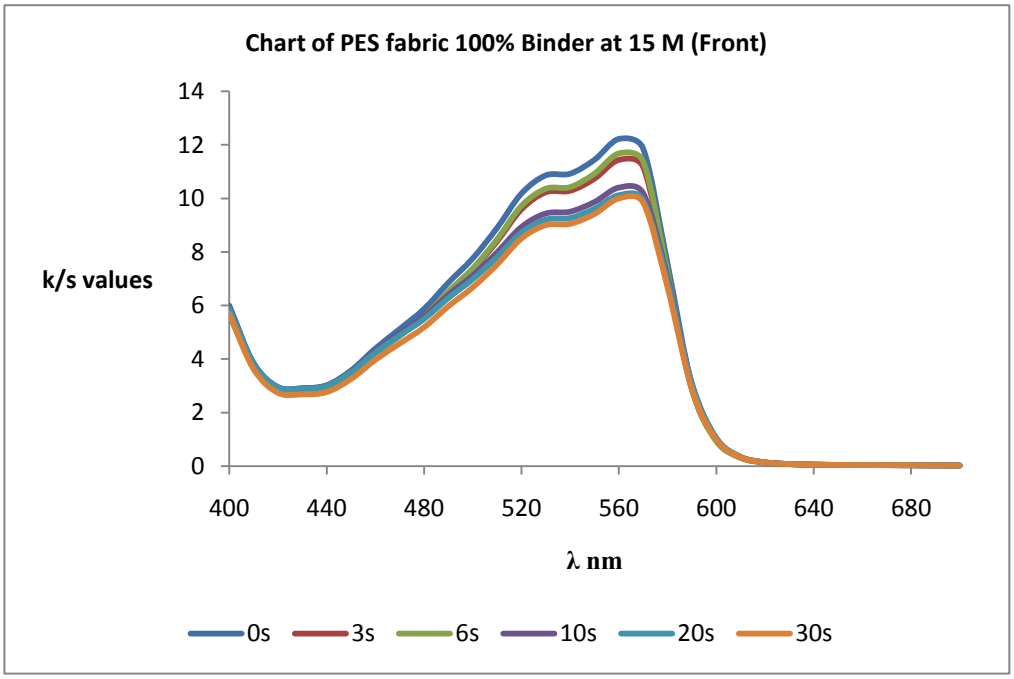


Fig 7.3.1(a) woven polyester fabric ,100% binder ,15M; front side

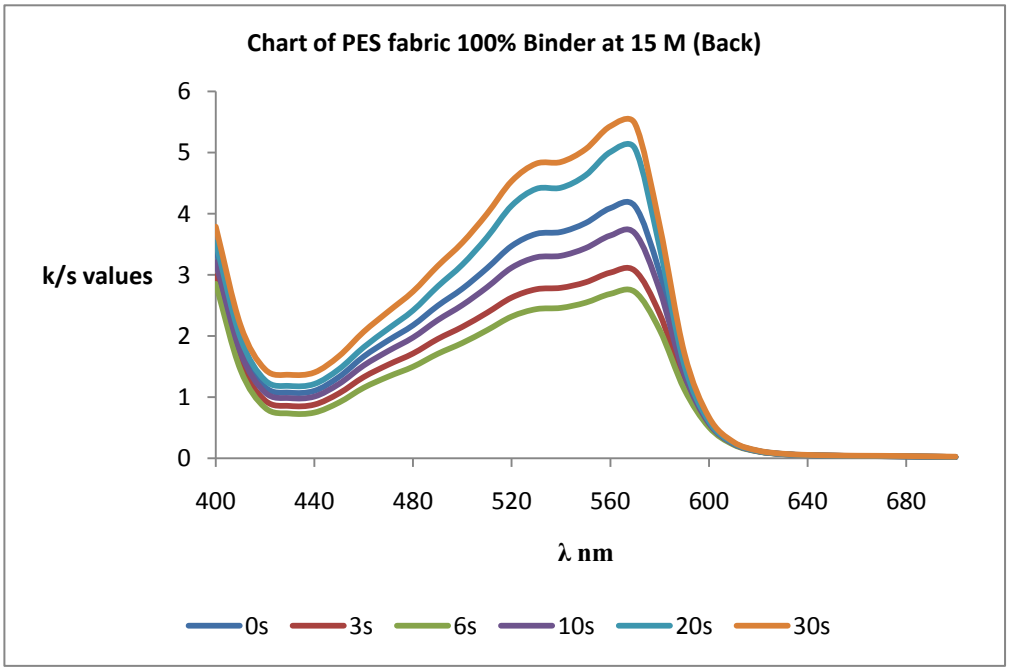


Fig 7.3.1(b) woven polyester fabric ,100% binder , 15%M ;back side

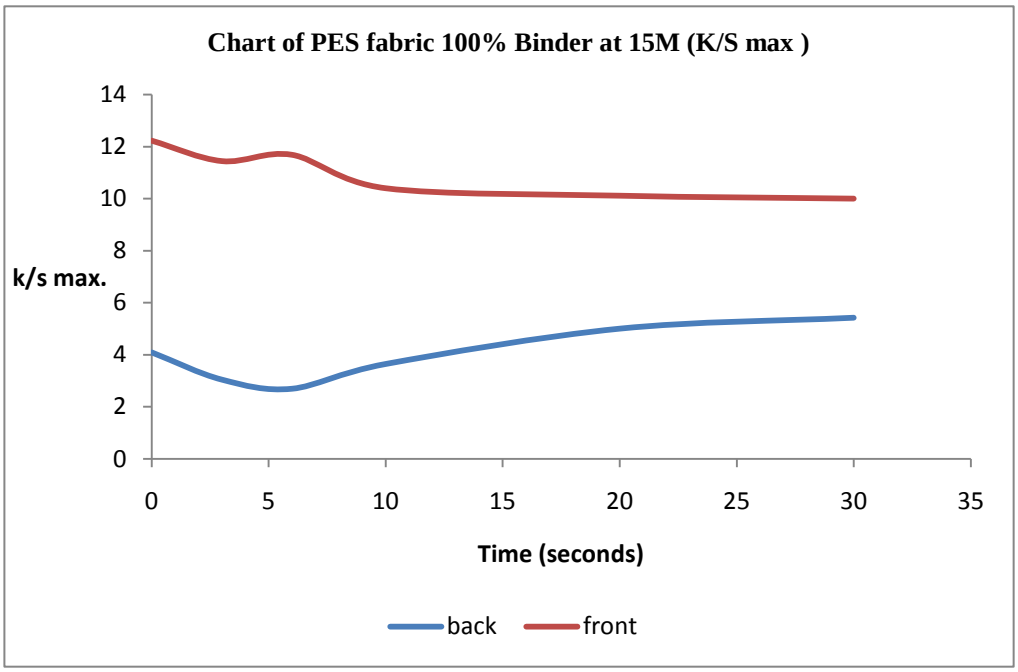


Fig 7.3.1.(c) woven polyestefabric ,100% binder ,15M k/s maximum

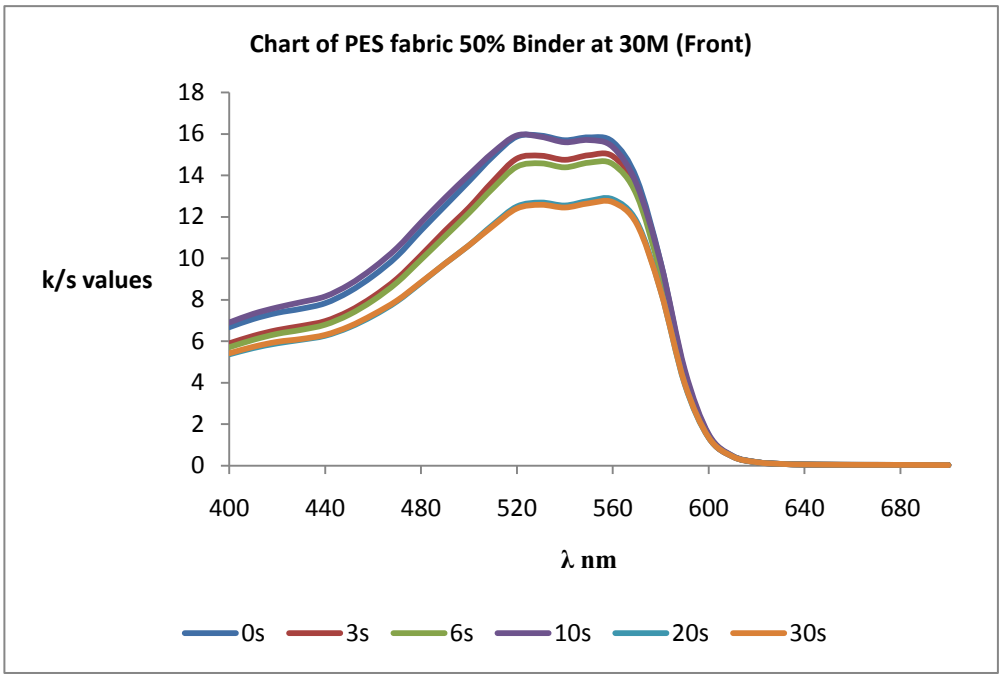


Fig 7.4: (a) woven polyester fabric 50% binder,30M; front side

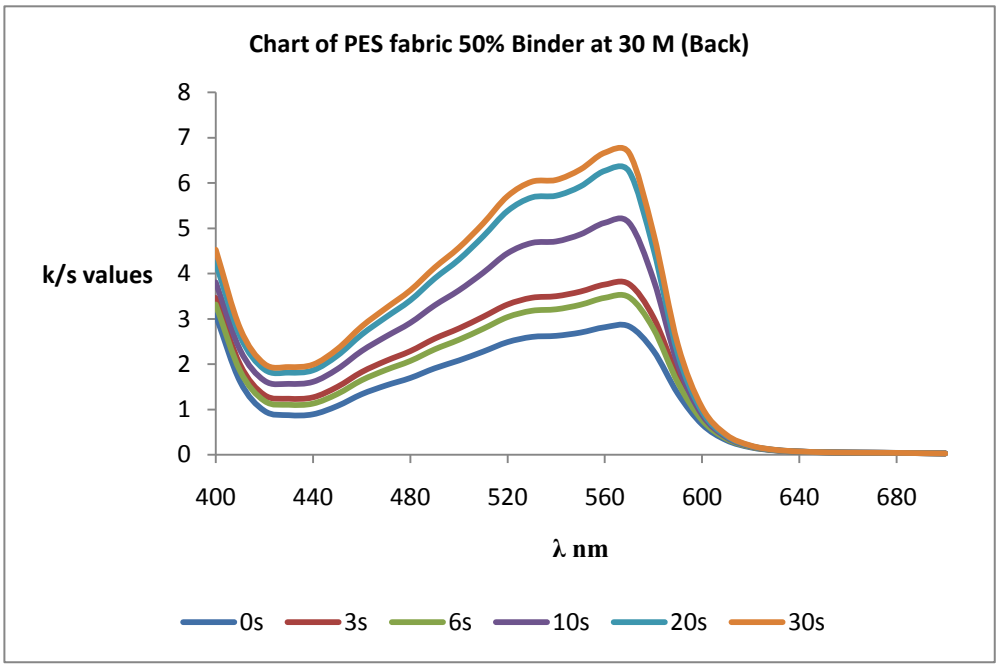


Fig 7.4:(b)woven polyester fabric ,50% binder,30M; back side

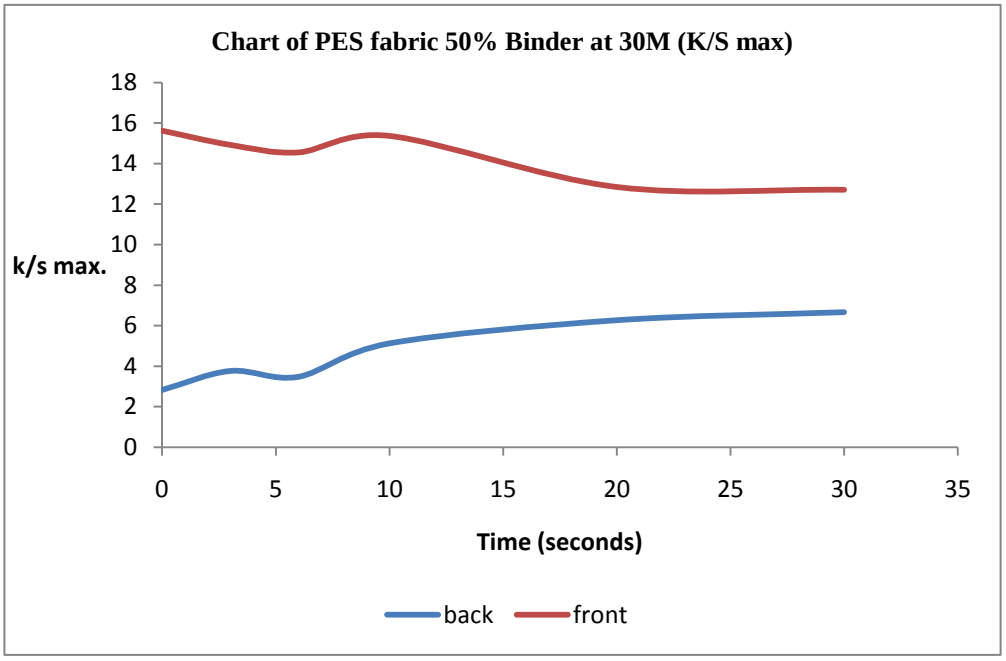


Fig 7.4:(c) woven polyester fabric ,50% binder,30M; k/s maximum

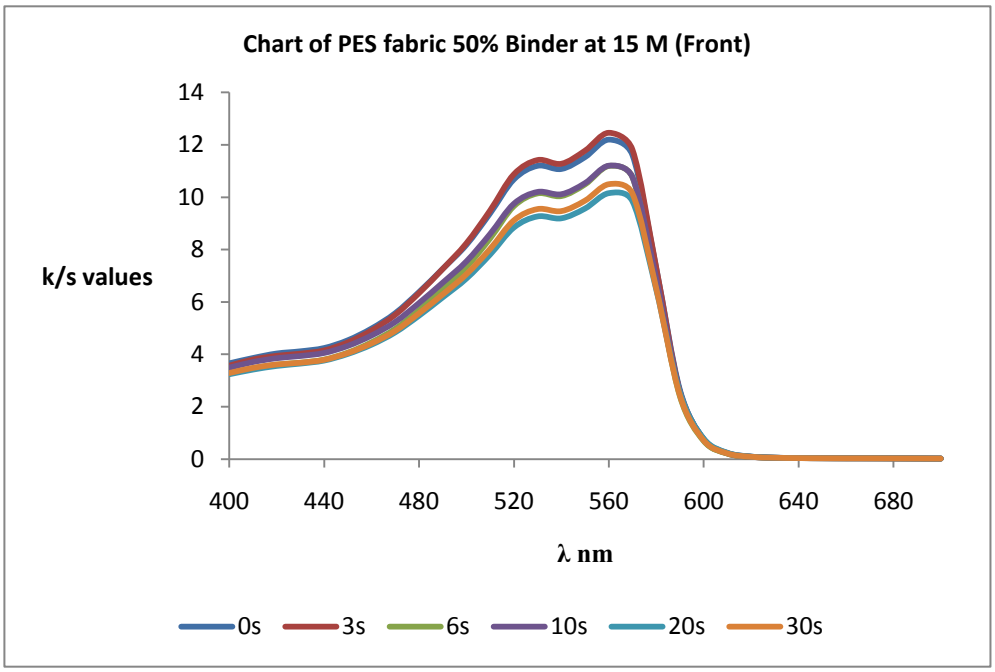


Fig 7.4.1:(a) woven polyester fabric,50% binder ,15M; front side

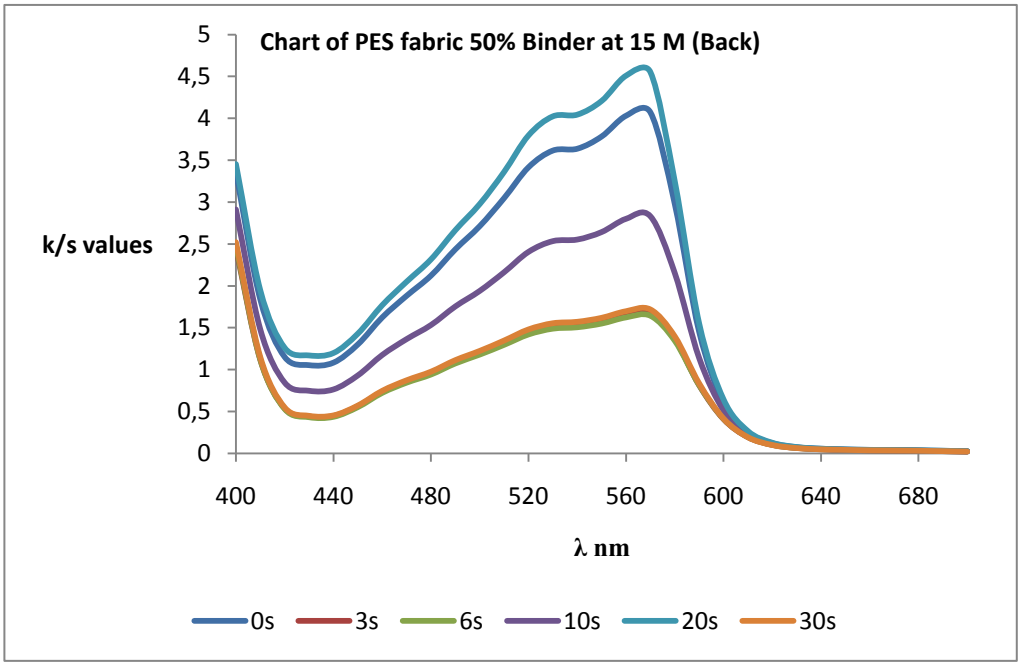


Fig 7.4.1(b) woven polyester fabric ,50%binder, 15M back side

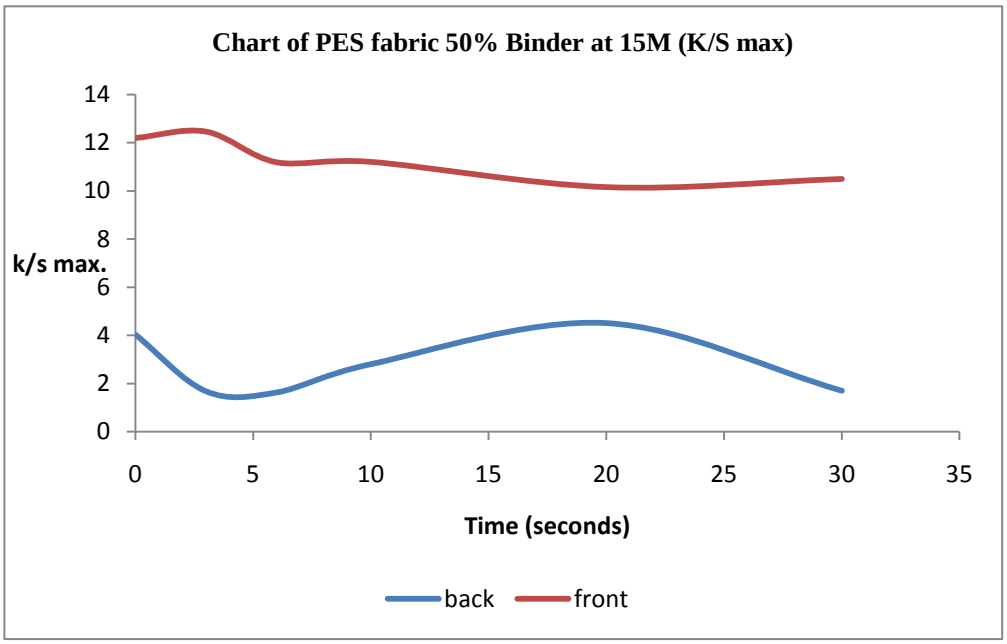


Fig 7.4.1.(c) woven polyester fabric ,50% binder ,15M k/smaximum

Spectrophotometry graphs for the Non –Woven polypropylene

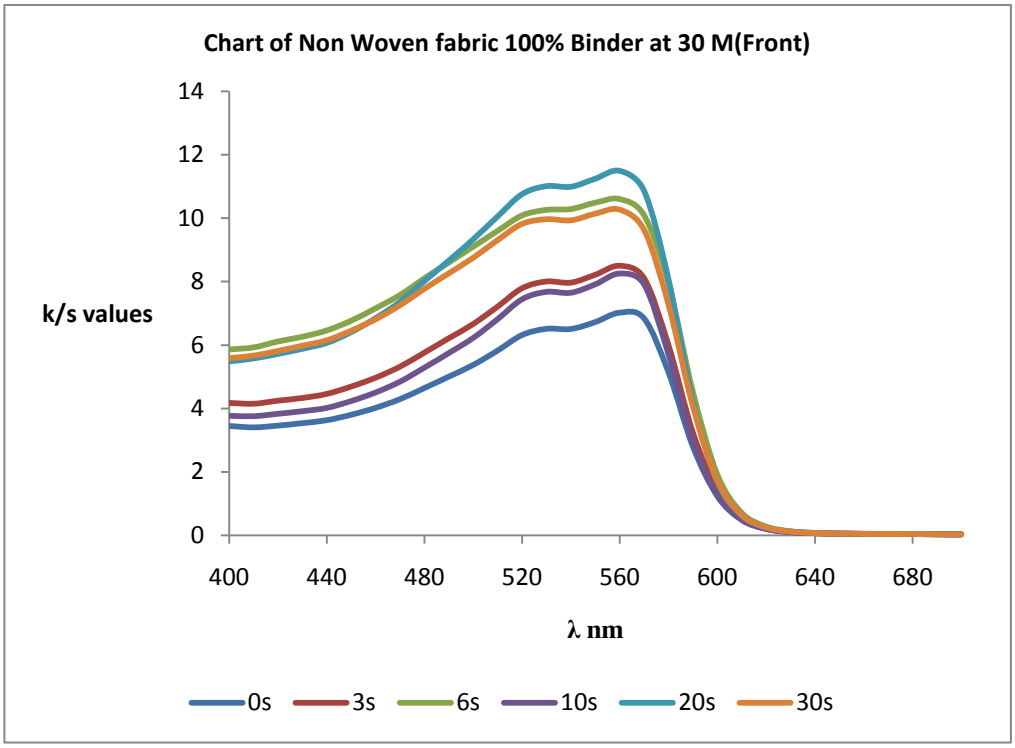


Fig 7.5: (a) non-woven polypropylene fabric ,100% binder ,30M; front side

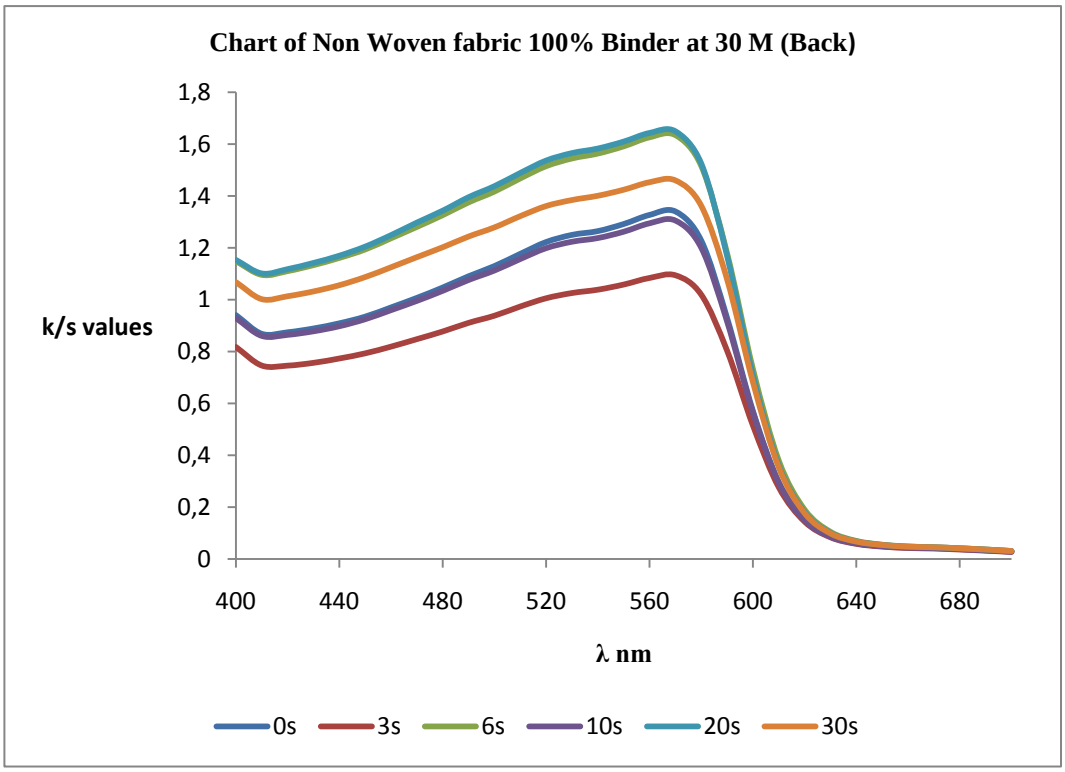


Fig 7.5 (b) non-woven polypropylene fabric,100% binder,30M;back side

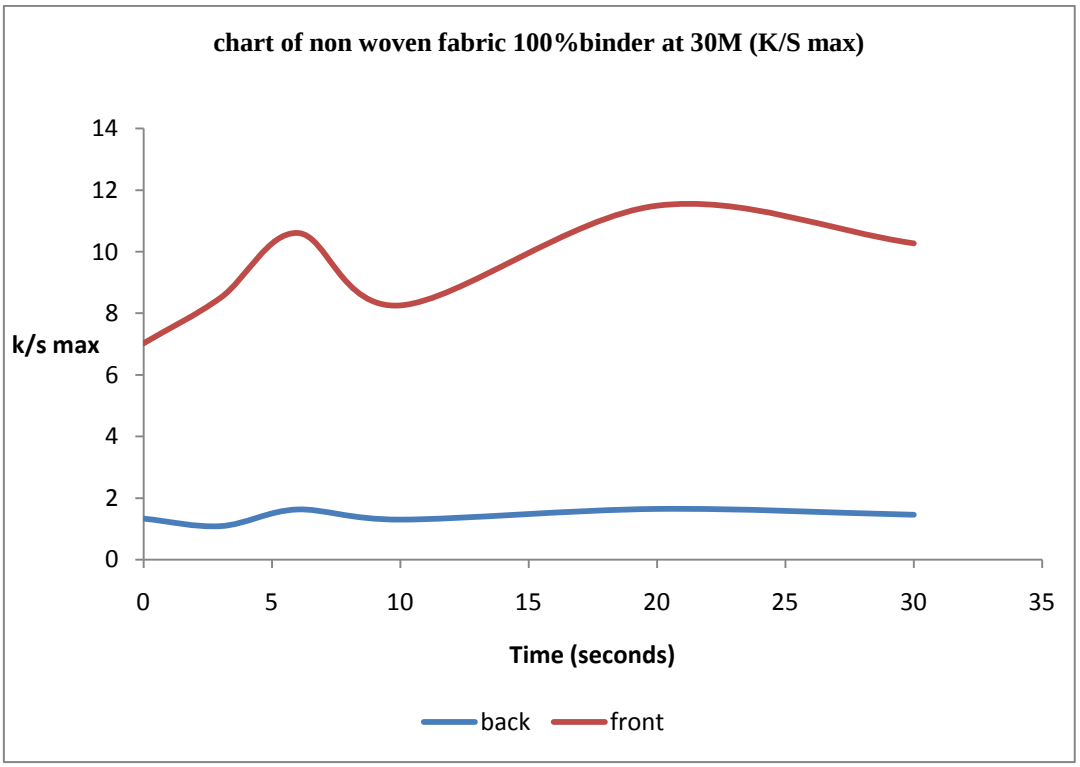


Fig 7.5 (c) non-woven polypropylene fabric, 100% binder,30M k/s maximum

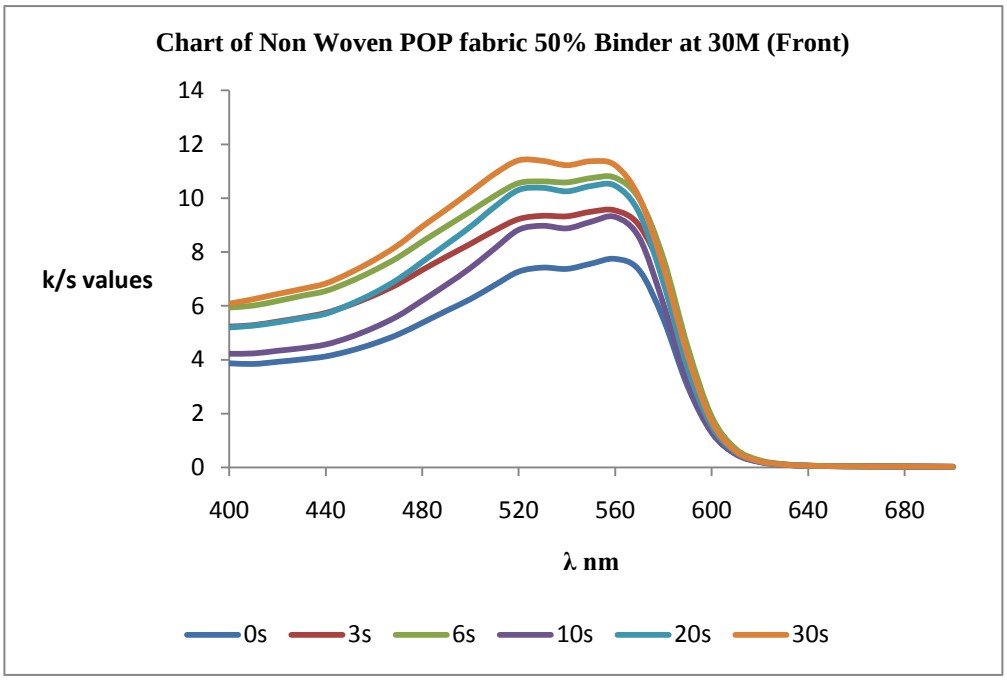


Fig 7.5.1: (a) non-woven polypropylene fabric, 50%binder, 30M ;front side

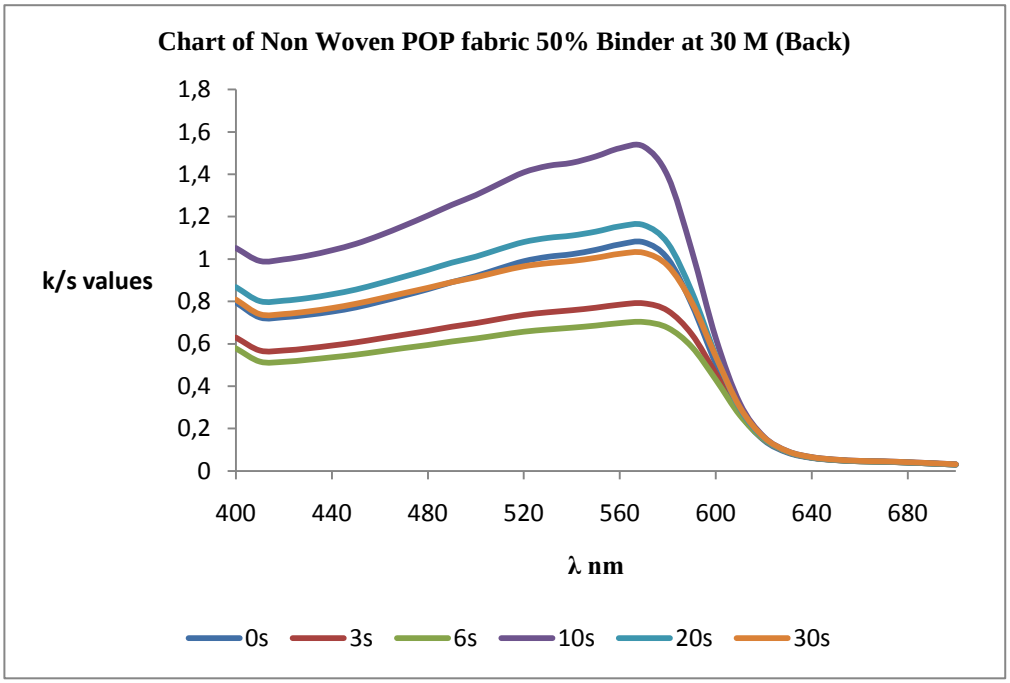


Fig 7.5.1:(b) non-woven polypropylene fabric ,50% binder ,30M;back side

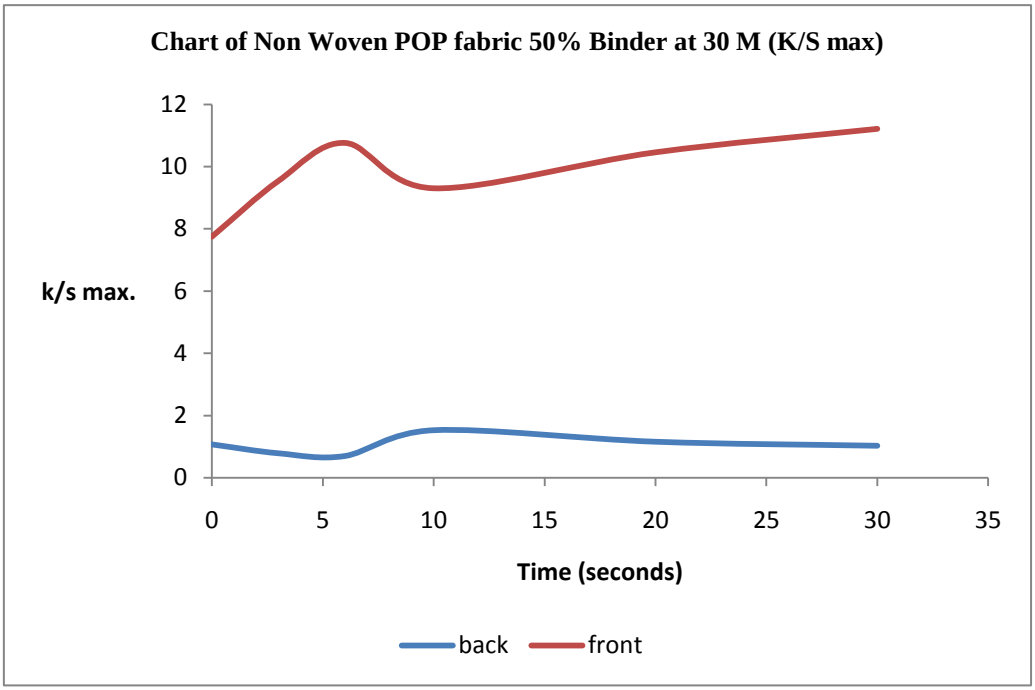


Fig 7.5.1 :(c) non-woven polypropylene fabric 50%binder ,30M;k/s maximum

4.6 Microscopy

SEM, images were observed to understand the alteration of surface morphology. In all cases the untreated samples showed the smooth surface, which generally means poor ability to hold water. The treated samples exhibit roughness on their surface, indicating that there are new reactive sites on the surface of textile.

Results

Micro-graphs at different magnification

Untreated samples :NWNPOP fabric

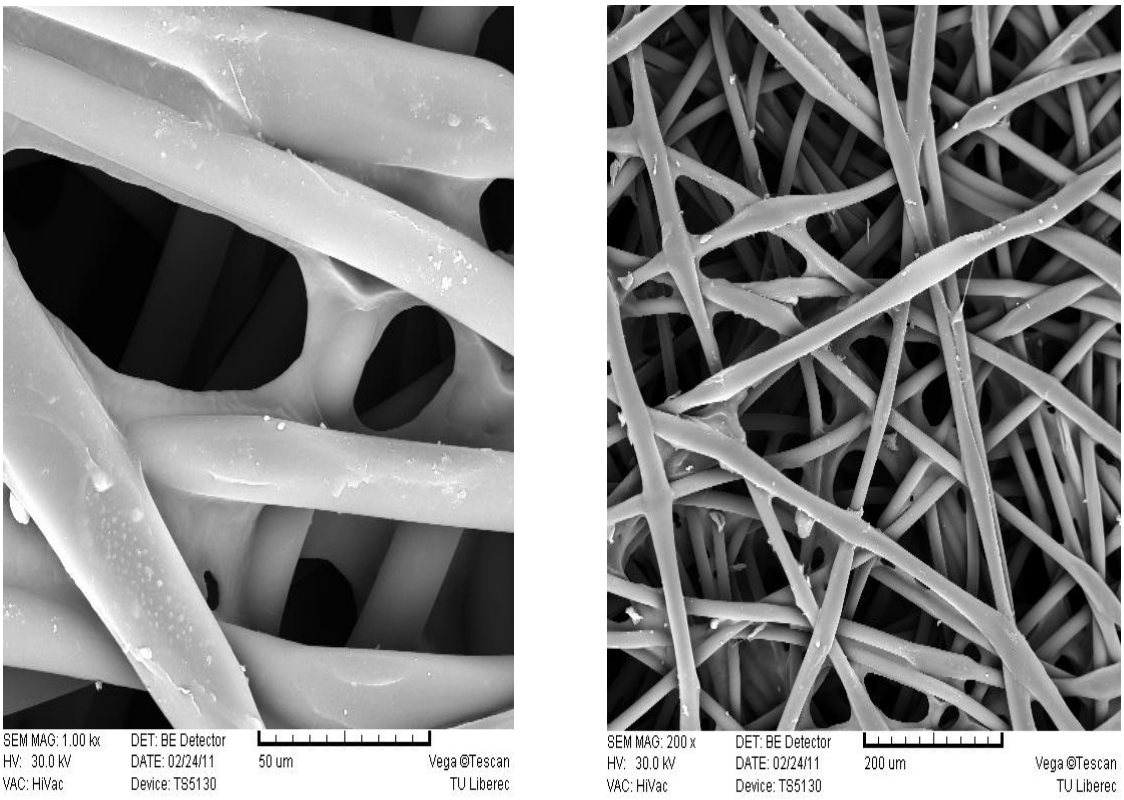


Fig 7.6 (a) NWN POP,100%binder; 30g/L; 0s; dry

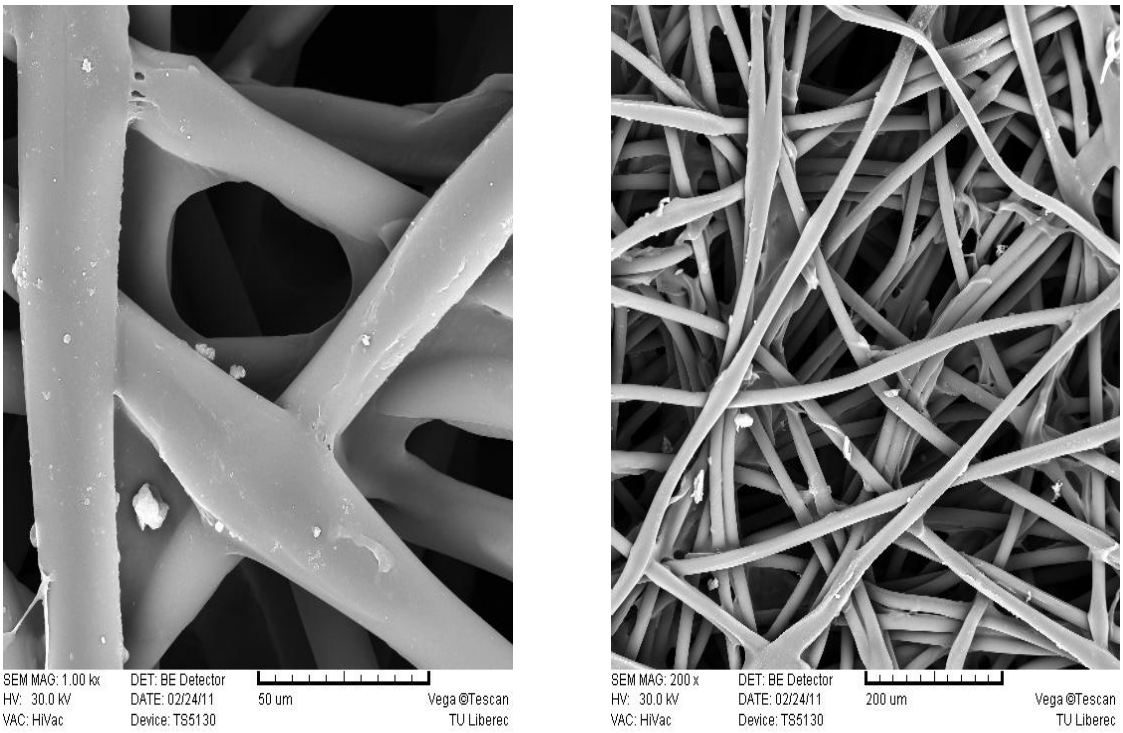


Fig7.6 (b) NWN POP,100%binder; 30g/L; 0s; printed

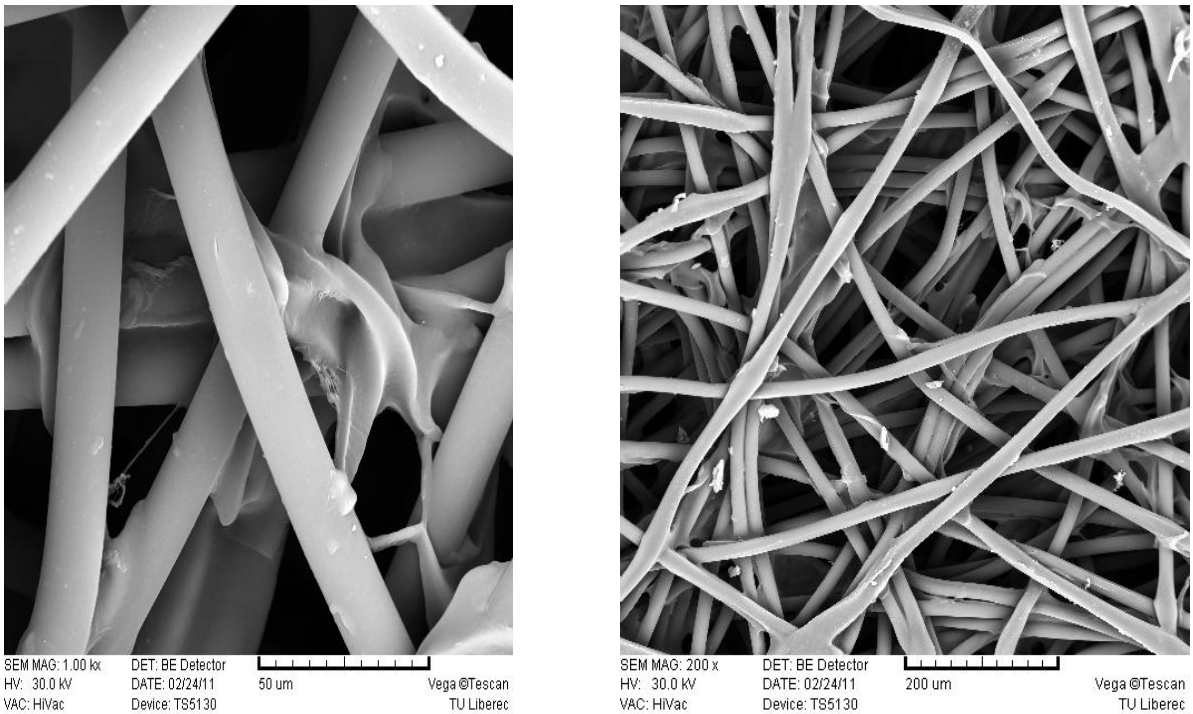


Fig 7.6:(c)NWN POP,100%binder; 30g/L; 0s

Treated sample :NWNPOP fabric

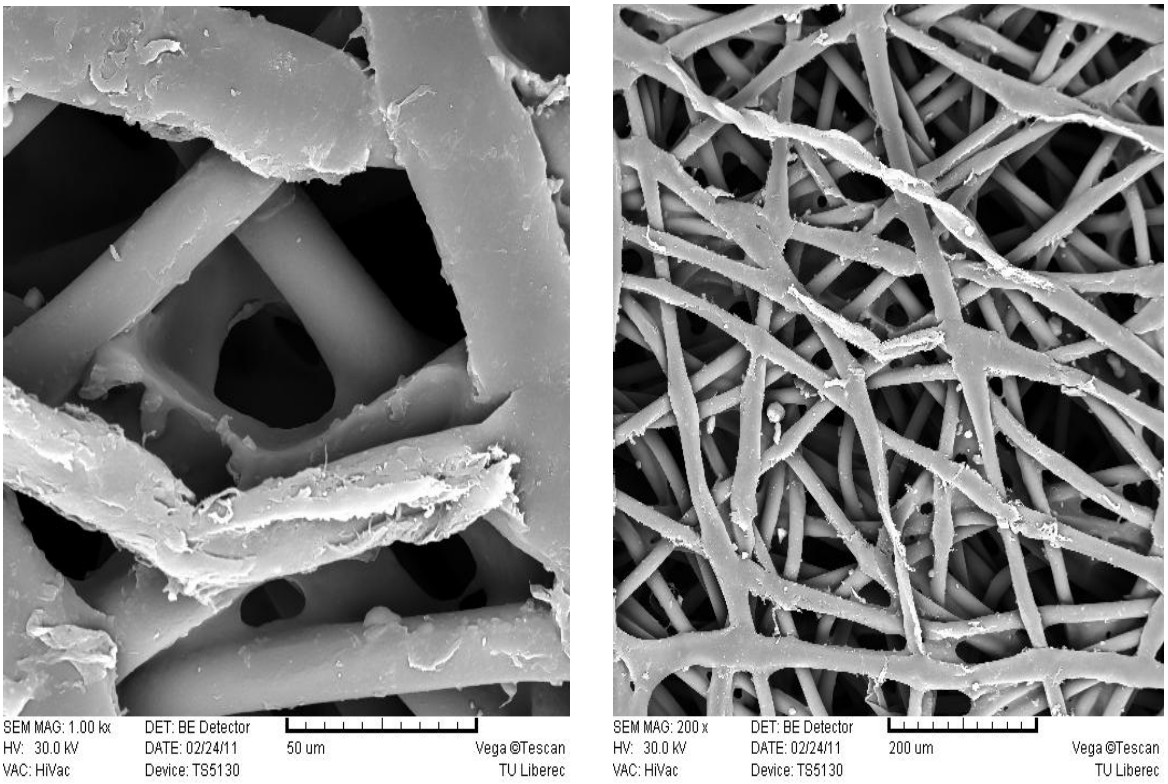


Fig 7.6.1(a) NWN POP;100%binder; 30g/L 30s;dry rubbing

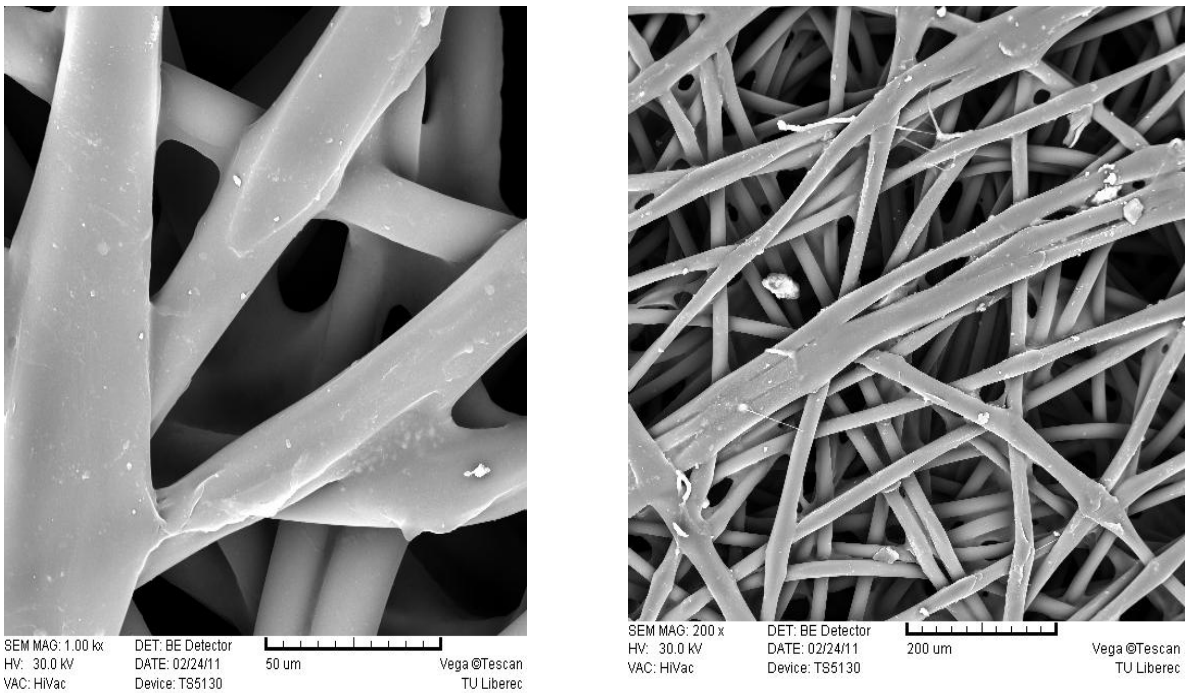


Fig 7.6.2:(b) NWN POP;100%binder; 30g/L ; 30s; printed

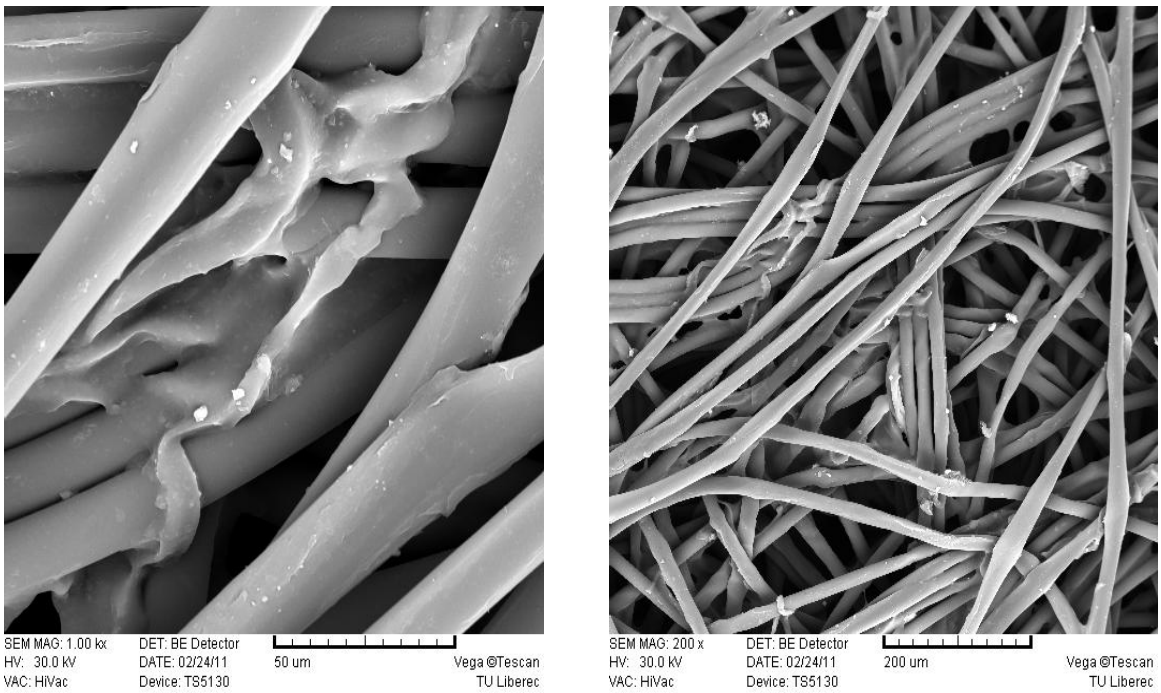


Fig 7.6.2 (c)NWN POP;100%binder; 30g/L ; 30s;wet rubbing

Untreated sample :WNPOP fabric

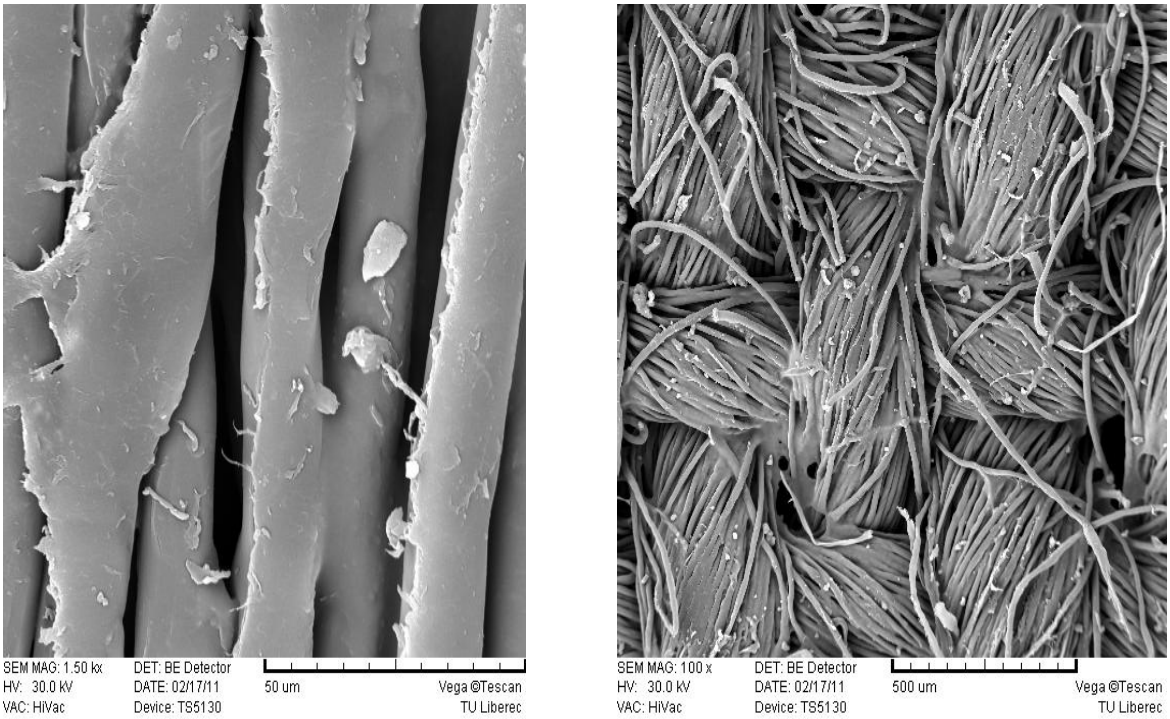


Fig 7.7 :(a) WNPOP ;100% binder;30 g/L 0s; dry

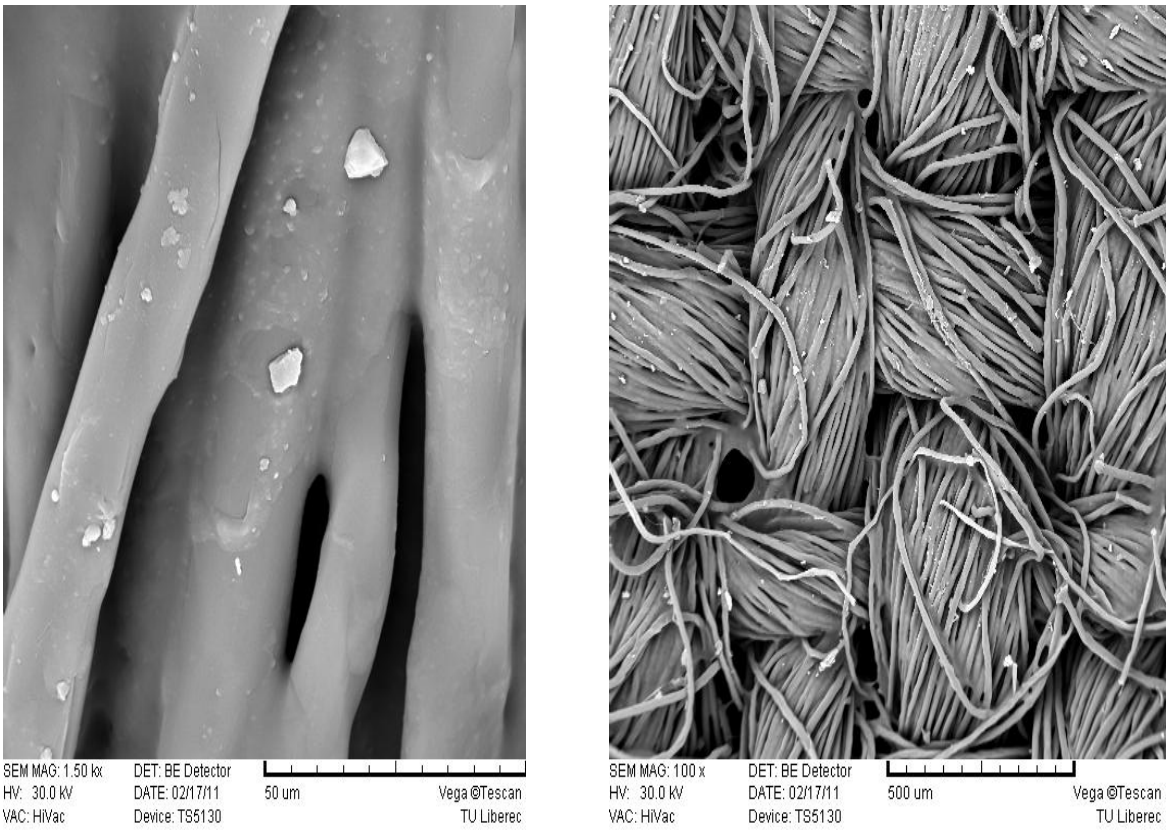


Fig 7.7: (b)WNPOP ;100% binder;30 g/L 0s ; Printed

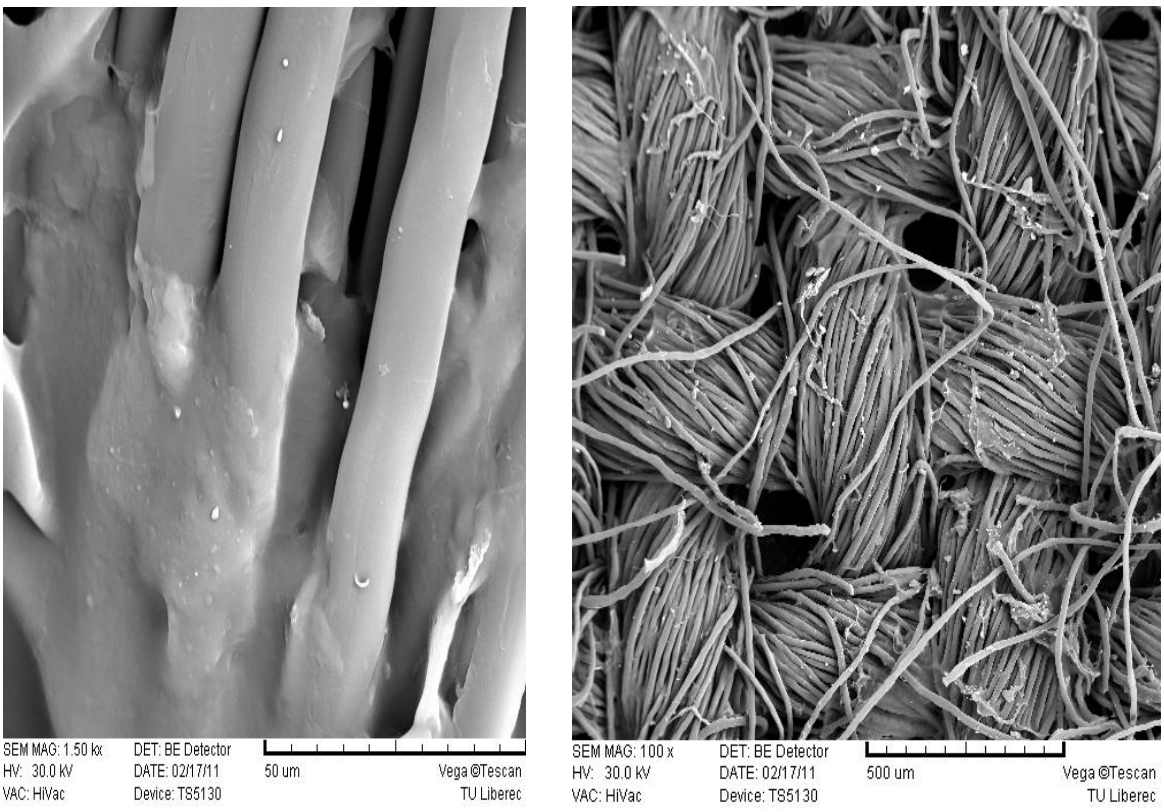


Fig 7.7:(c) 100% binder;30 g/L 0s ; wet rubbing

Treated samples : WNPOP fabric

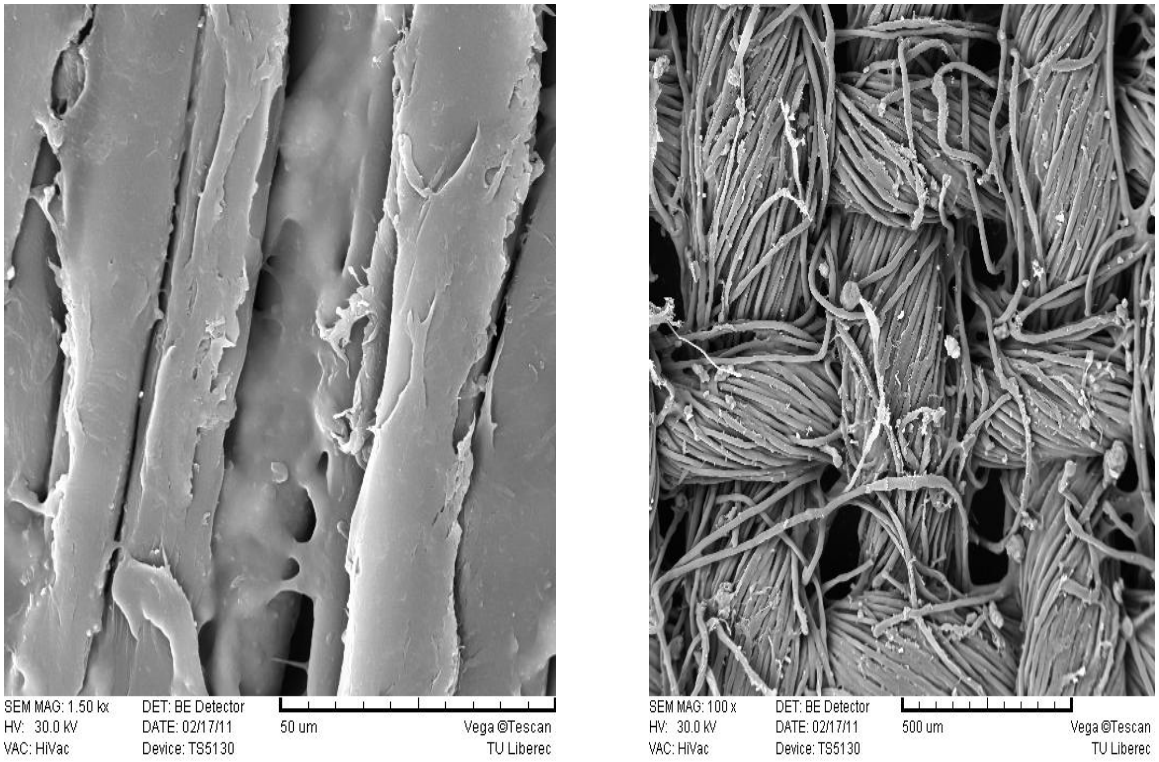


Fig 7.7.1:(a) WNPOP ;100% binder;30 g/L; 30s; dry rubbing

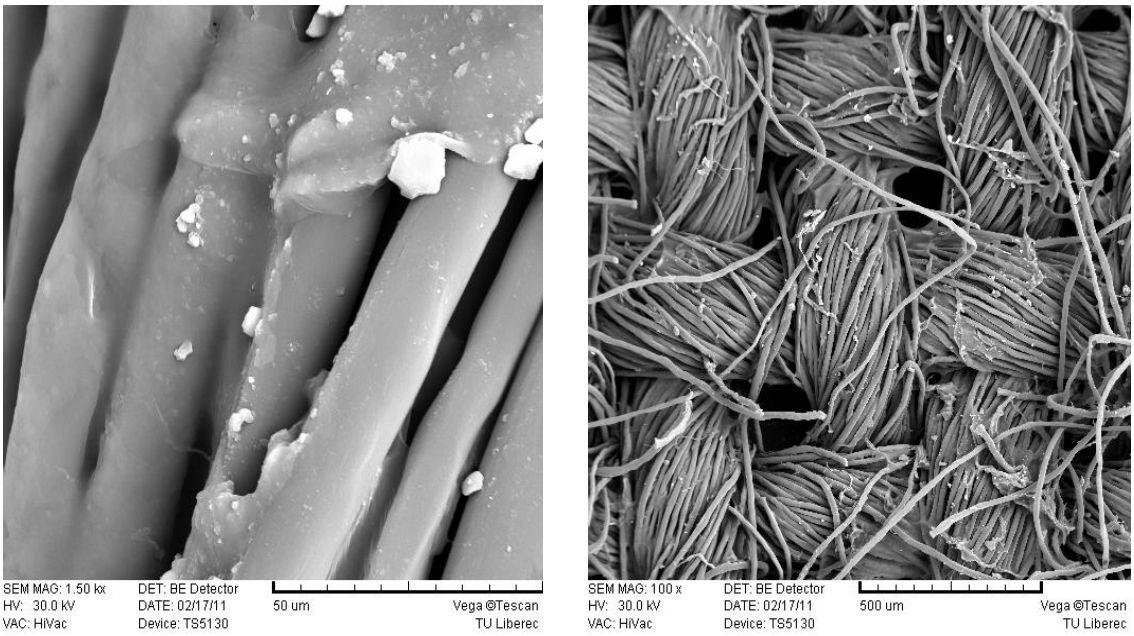


Fig 7.7.1 (b) WNPOP ;100% binder;30 g/L; 30s; printed

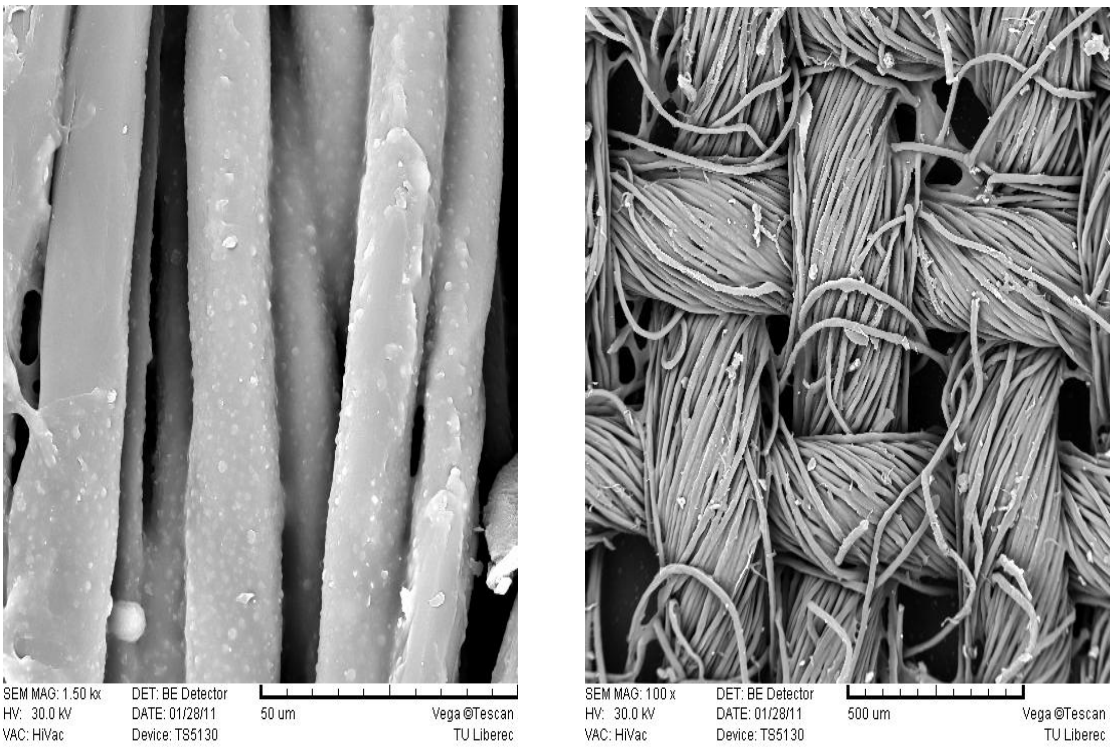


Fig 7.7.1.(c) WNPOP ;100% binder;30 g/L; 30s;wet rubbing

Untreated samples ;WNPES fabric

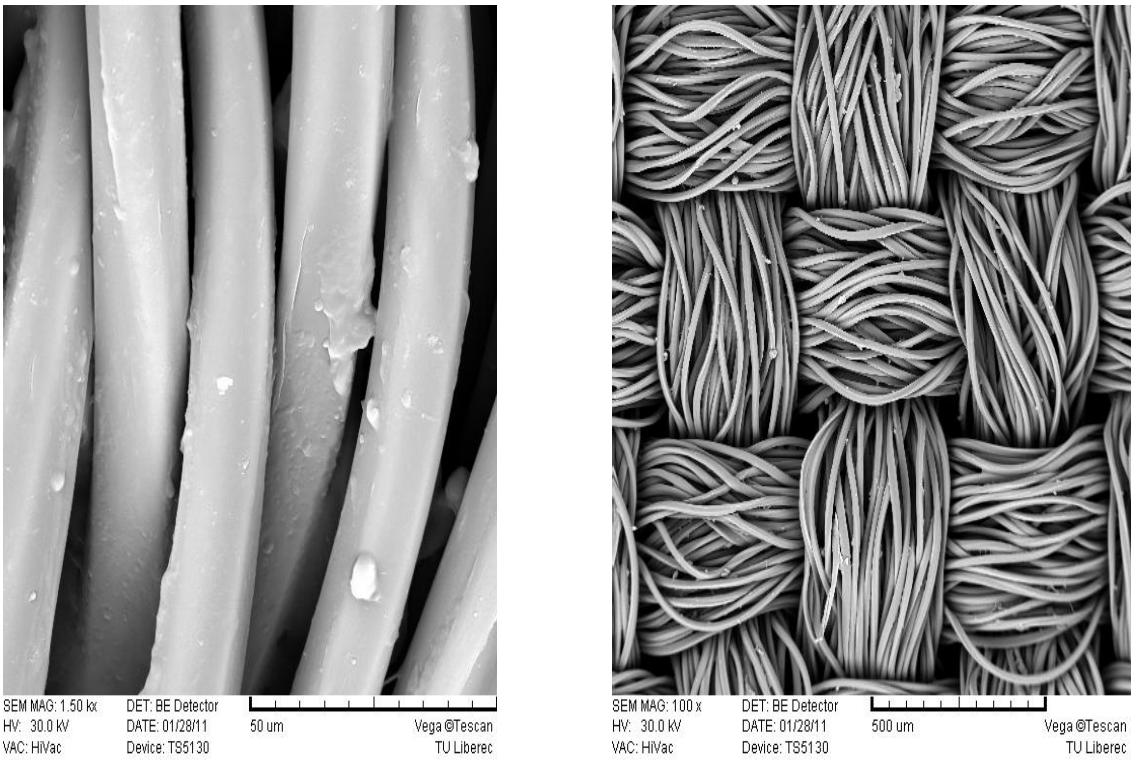


Fig 7.8 (a) WNPES'100%binder; 30g/L; 0s; Dry rubbing

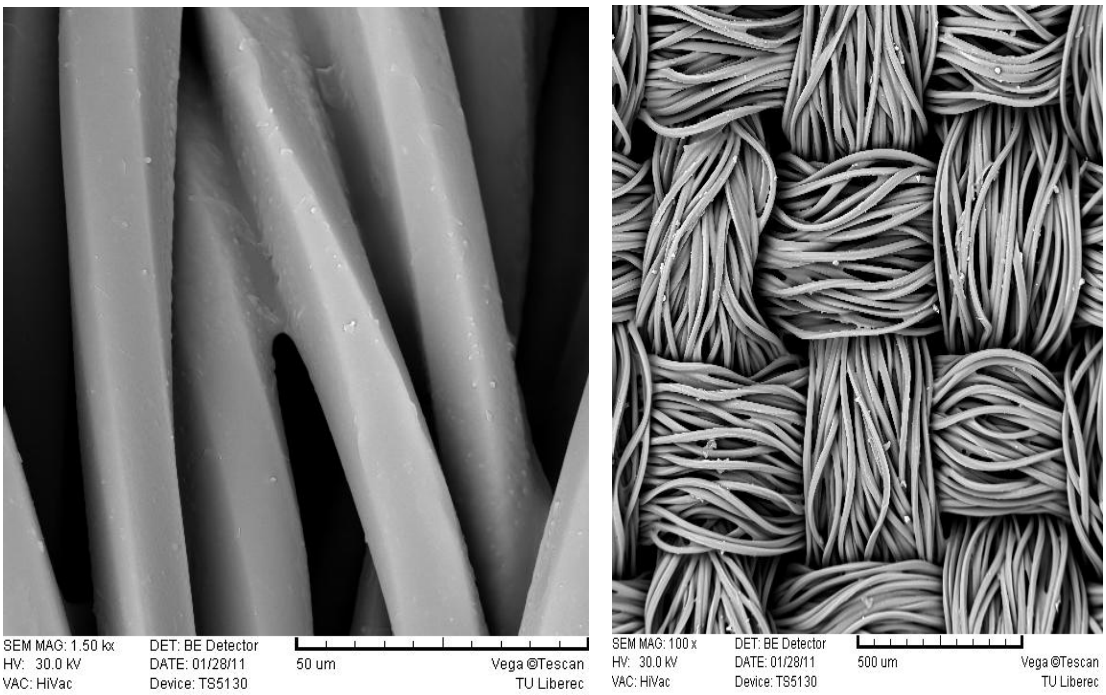


Fig 7.8 :(b) WNPES'100%binder; 30g/L; 0s; printed

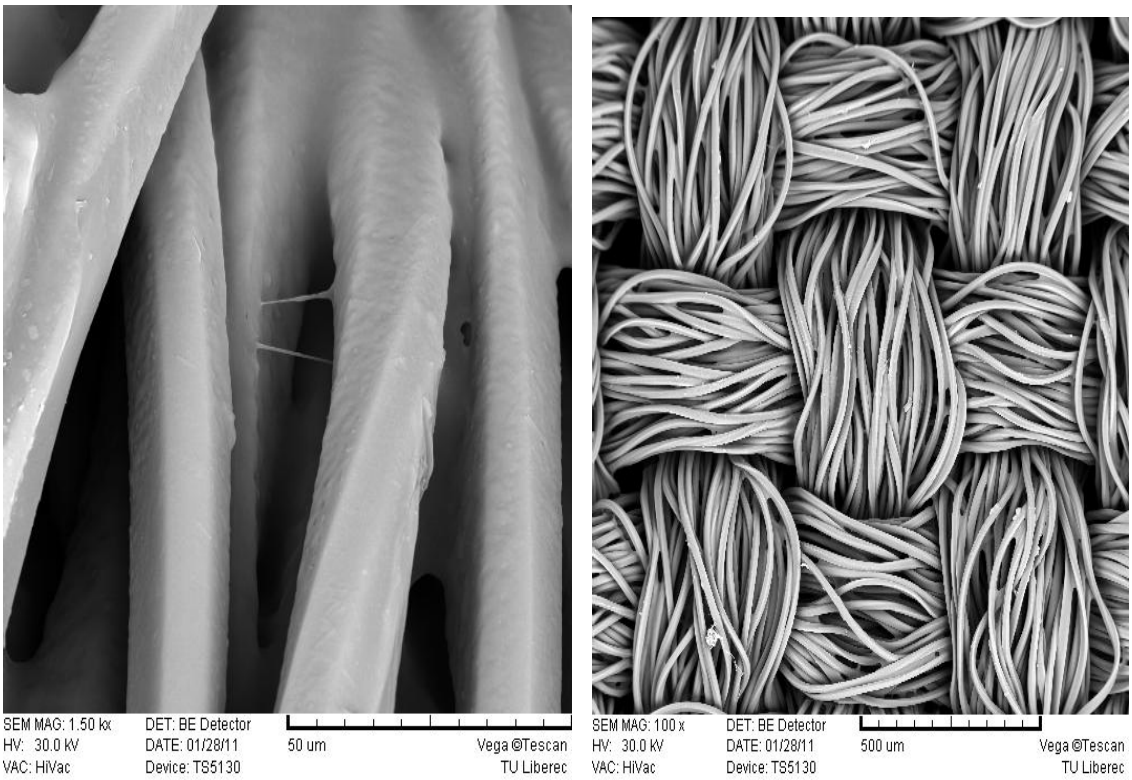


Fig 7.8 :(c) WNPES'100%binder; 30g/L; 0s; wet rubbing

Treated samples :WNPES fabric

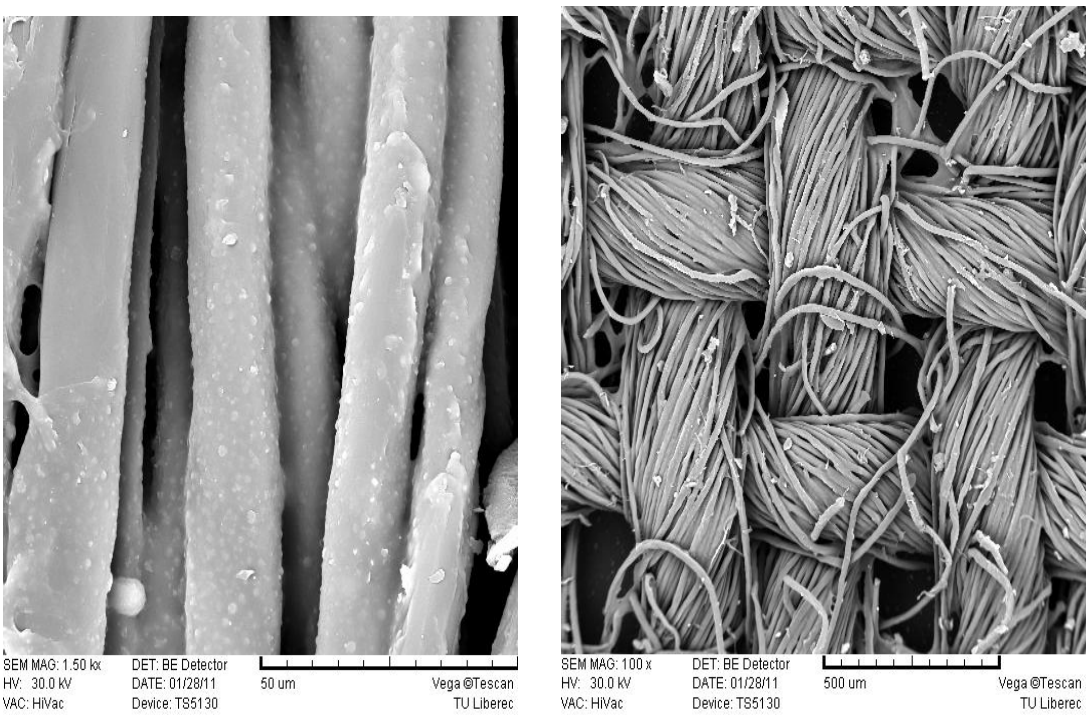
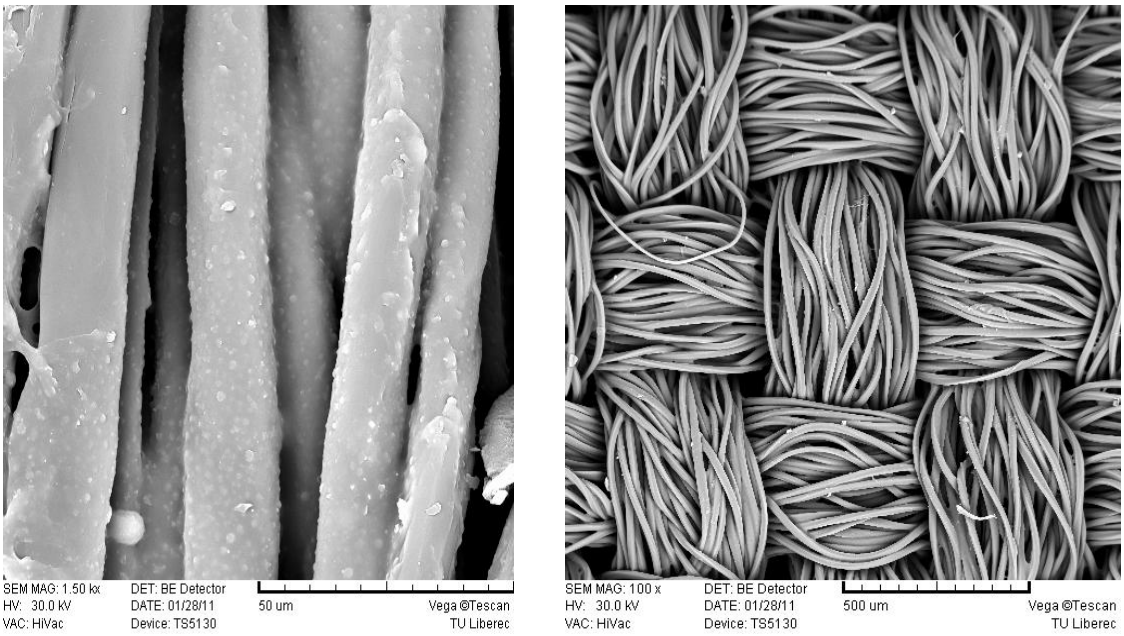


Fig 7.8.1:(a) WNPES;100% binder;30g/L; 30s;dry rubbing



Printed **Fig 7.8.1:(b) WNPES;100% binder;30g/L; 30s; printed**

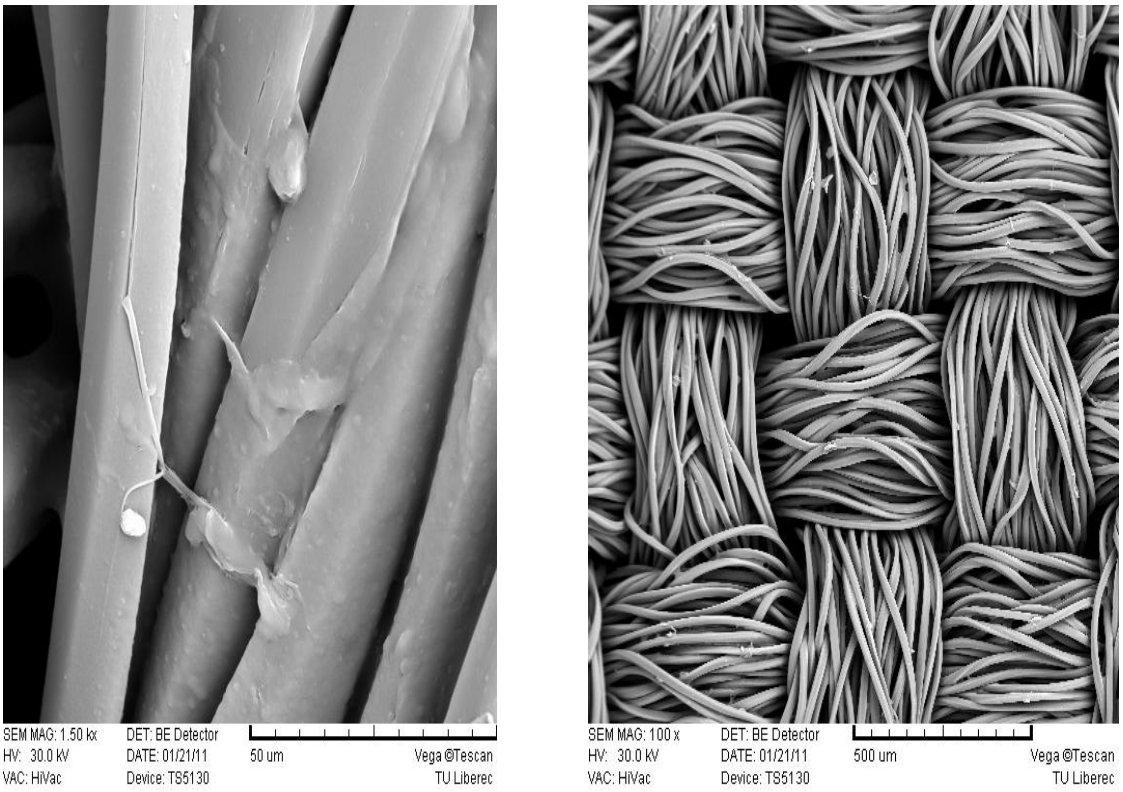


Fig 7.8.1:(c) WNPES;100% binder;30g/L; 30s; wet rubbing

4.7 Optical Microscopy

Discussion

ImageJ was used as a tool for this analysis.

Results obtained from the optical microscope also exhibited positive effect of plasma treatment. Untreated sample gave low color intensity whereas the treated samples gave high color intensity. Fastness properties on the textile material were proven by the cross-sectional views. From these views it is evident that the color intensity increases at high contents of pigment enforced with full binding system.

Again the untreated samples showed low intensity and the treated samples showed high intensity. This is due to the activation provided by the treatment and the cross-linking groups contained in the binder.

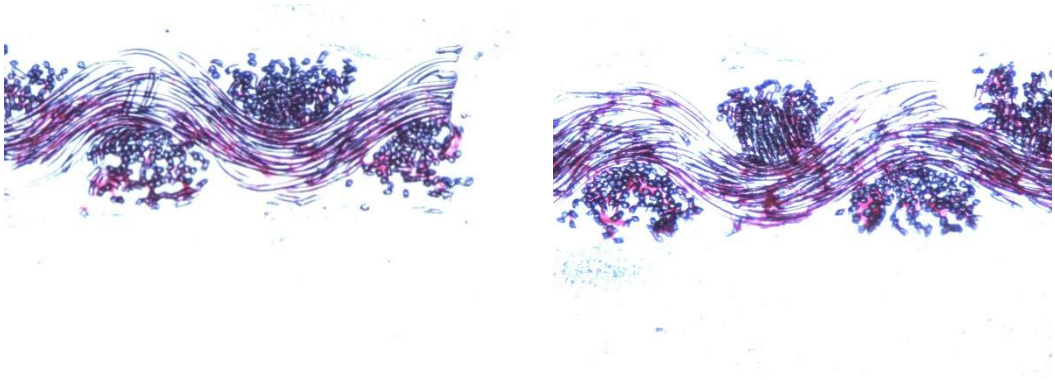


Fig 7.9:crossectional view of WNPOP.15g/L ; 0S : and POP.15g/L; 30s

5 Conclusion

Most polymer surfaces require a certain extent of activation to allow further processing. Unlike conventional wet processes which penetrate deeply into fibers, plasma only react with the fabric surface and will not affect the internal structure of the fibers .Plasma technology is used to modify the chemical structure as well as the topography of the textile material surface. Shifting in XPS Peaks indicate different binding states present. For example PP is predominantly alkane, (-c-c-) bond in its structure .Carbon –oxygen bonding is clearly present after plasma discharge process. Hence plasma treatment is able to affect the surface energy and contact angle of polymeric materials. In principle (according to the definition) plasma is not in contact with the work piece during the plasma treatments The fluxes of ions and active species with their energies is the key point of the surface treatment .The more time taken by the fabric under plasma treatment the better printability of materials as our results revealed the effect .For the non-woven fabric it is noted that fastness properties are good depending on the choice of the material being utilised. Pigment printing has good fastness properties to rubbing.

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